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THE

PHYSICAL REVIEW

THE SPECTRUM OF SCATTERED X-RAYS[1]

BY ARTHUR H. COMPTON

ABSTRACT

The spectrum of molybdenum $K\alpha$ rays scattered by graphite at 45°, 90° and 135° has been compared with the spectrum of the primary beam. A primary spectrum line when scattered is broken up into two lines, an "unmodified" line whose wave-length remains unchanged, and a "modified" line whose wave-length is greater than that of the primary spectrum line. Within a probable error of about 0.001 A, the difference in the wave-lengths $(\lambda-\lambda_0)$ increases with the angle θ between the primary and the scattered rays according to the quantum relation $(\lambda-\lambda_0)=\lambda(1-\cos\theta)$, where $\lambda=h/mc=0.0242$ A. This wave-length change is confirmed also by absorption measurements. The modified ray does not seem to be as homogeneous as the unmodified ray; it is less intense at small angles and more intense at large angles than is the unmodified ray.

An x-ray tube of small diameter and with a water-cooled target is described, which is suitable for giving intense x-rays.

THE WRITER has recently proposed a theory of the scattering of x-rays, based upon the postulate that each quantum of x-rays is scattered by an individual electron.[2,3] The recoil of this scattering electron, due to the change in momentum of the x-ray quantum when its direction is altered, reduces the energy and hence also the frequency of the quantum of radiation. The corresponding increase in the wave-length of the x-rays due to scattering was shown to be

$$\lambda-\lambda_0=\gamma(1-\cos\theta) \qquad (1)$$

where λ is the wave-length of the ray scattered at an angle θ with the primary ray whose wave-length is λ_0, and

$$\gamma=h/mc=0.0242 \text{ A}$$

where h is Planck's constant, m is the mass of the electron and c the

[1] A report on this work was presented before the American Physical Society, Apr. 21, 1923 (Phys. Rev. **21**, 715, 1923).

[2] A. H. Compton, Bull. Nat. Res. Coun., No. 20, p. 18 (October 1922); Phys. Rev. **21**, 207 (abstract) (Feb. 1923); Phys. Rev. **21**, 483 (May, 1923).

[3] Cf. also P. Debye, Phys. Zeitschr. **24**, 161 (April 15, 1923)

velocity of light. It is the purpose of this paper to present more precise experimental data than has previously been given regarding this change in wave-length when x-rays are scattered.

Apparatus and method. For the quantitative measurement of the change in wave-length it was clearly desirable to employ a spectroscopic method. In view of the comparatively low intensity of scattered x-rays, the apparatus had to be designed in such a manner as to secure the maximum intensity in the beam whose wave-length was measured. The arrangement of the apparatus is shown diagrammatically in Fig. 1. Rays proceeded from the molybdenum target T of an x-ray tube to the graphite

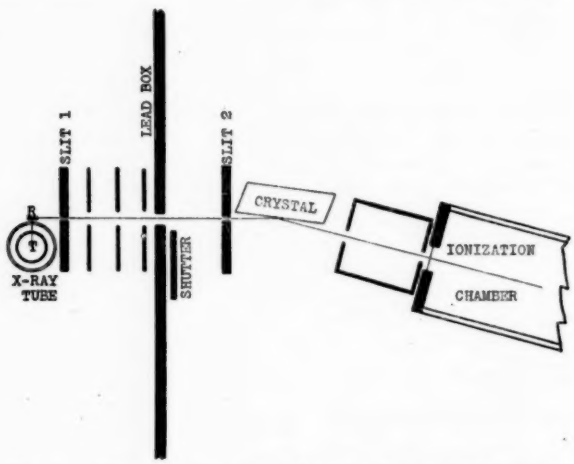

Fig. 1. Measuring the wave-length of scattered x-rays.

scattering block R, which was placed in line with the slits 1 and 2. Lead diaphragms, suitably disposed, prevented stray radiation from leaving the lead box that surrounded the x-ray tube. Since the slit 1 and the diaphragms were mounted upon an insulating support, it was possible to place the x-ray tube close to the slit without danger of puncture. The x-rays, after passing through the slits, were measured by a Bragg spectrometer in the usual manner.

The x-ray tube was of special design. A water-cooled target was mounted in a narrow glass tube, as shown in Fig. 2, so as to shorten as much as possible the distance between the target T and the radiator R. This distance in the experiments was about 2 cm. When 1.5 kw was dissipated in the x-ray tube, the intensity of the rays reaching the radiator was thus 125 times as great as it would have been if a standard Coolidge tube with a molybdenum target had been employed. The electrodes for this tube were very kindly supplied by the General Electric Company.

In the final experiments the distance between the slits was about 18 cm, their length about 2 cm, and their width about 0.01 cm. Using a crystal of calcite, this made possible a rather high resolving power even in the first order spectrum.

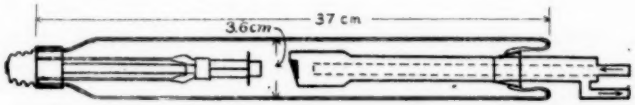

Fig. 2. X-ray tube.

Spectra of scattered molybdenum rays. Results of the measurements, using slits of two different widths, are shown in Figs. 3 and 4. Curves A represent the spectrum of the Kα line, and curves B, C and D are the spectra of this line after being scattered at angles of 45°, 90° and 135° respectively with the primary beam. While in Fig. 4 the experimental

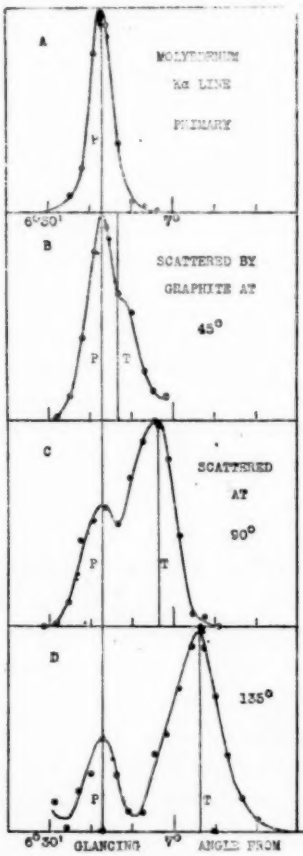

Fig. 3

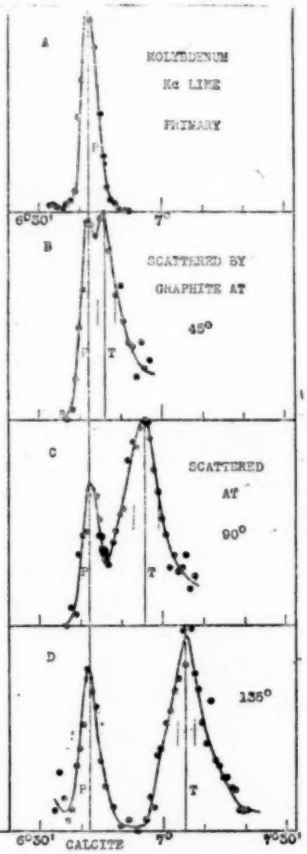

Fig. 4

points are a little erratic, it may be noted that in this case the intensity of the x-rays is only about 1/25,000 as great as if the spectrum of the primary beam were under examination, so that small variations produce a relatively large effect.

It is clear from these curves that when a homogeneous x-ray is scattered by graphite it is separated into two distinct parts, one of the same wave-length as the primary beam, and the other of increased wave-length. Let us call these the *modified* and the *unmodified* rays respectively. In each curve the line P is drawn through the peak of the curve representing the primary line, and the line T is drawn at the angle at which the scattered line should appear according to Eq. (1). In Fig. 4, in which the settings were made with the greater care, within an experimental error of less than 1 minute of arc, or about 0.001 A, the peak of the unmodified ray falls upon the line P and the peak of the modified ray falls upon the line T. The wave-length of the modified ray thus increases with the scattering angle as predicted by the quantum theory, while the wave-length of the unmodified ray is in accord with the classical theory.

There is a distinct difference between the widths of the unmodified and the modified lines. A part of the width of the modified line is due to the fact that the graphite radiator R subtends a rather large angle as viewed from the target T, so that the angles at which the rays are scattered to the spectrometer crystal vary over an appreciable range. As nearly as I can estimate, the width at the middle of the modified line due to this cause is that indicated in Fig. 4 by the two short lines above the letter T. It does not appear, however, that this geometrical consideration is a sufficient explanation for the whole increased width of the modified line, at least for the rays scattered at 135°. It seems more probable that the modified line is heterogeneous, even in a ray scattered at a definite angle.

The unmodified ray is usually more prominent in a beam scattered at a small angle with the primary beam, and the modified ray more prominent when scattered at a large angle. A part of the unmodified ray is doubtless due to regular reflection from the minute crystals of which the graphite is composed. If this were the only source of the unmodified ray, however, we should expect its intensity to diminish more rapidly at large angles than is actually observed. The conditions which determine the distribution of energy between these two rays are those which determine whether an x-ray shall be scattered according to the simple quantum law or in some other manner. I have studied this distribution experimentally by another method, and shall discuss

it in another paper;[4] but the reasons underlying this distribution are puzzling.

Experiments with shorter wave-lengths. These experiments have been performed using a single wave-length, $\lambda = 0.711$ A. In this case we find for the modified ray a change in wave-length which increases with the angle of scattering exactly in the manner described by Eq. (1). While these experiments seem conclusive, the evidence would of course be more complete if similar experiments had been performed for other wave-lengths. Preliminary experiments similar to those here described have been performed using the K radiation from tungsten, of wave-length about 0.2 A. This work has shown a change in wave-length of the same order of magnitude as that observed using the molybdenum Kα line. Furthermore, as described in earlier papers,[5] absorption measurements have confirmed these results as to order of magnitude over a very wide range of wave-lengths. This satisfactory agreement between the experiments and the theory gives confidence in the quantum formula (1) for the change in wave-length due to scattering. There is, indeed, no indication of any discrepancy whatever, for the range of wave-length investigated, when this formula is applied to the wave-length of the modified ray.

WASHINGTON UNIVERSITY,
SAINT LOUIS,
May 9, 1923.

[4] A. H. Compton, Phil. Mag. (in printer's hands)
[5] Cf. e.g., A. H. Compton, Phys. Rev. **21**, pp. 494–6 (1923)

AN EXPERIMENTAL CHECK OF THE OPTICAL THEORY OF X-RAY REFLECTION

By Paul Kirkpatrick

Abstract

Effective absorption coefficient of rock salt for first order (100) reflected x-radiations has been determined from a study of transmission reflection as a function of crystal thickness, according to the method of Bragg, James, and Bosanquet, for five *wave-lengths between .24 A and .59 A*. The results are well represented by the equation $\mu = 189\ \lambda^{3.9} + .43$, where λ is in Angström units. The secondary *extinction coefficient*, due to irregularities of the crystal, was also obtained by subtracting the ordinary absorption coefficient μ_0 from μ, and was found to conform to the equation $\epsilon = 190\ \lambda^{4.6}$. The primary extinction coefficient was assumed to be negligible.

Variation of the x-ray reflecting power of (100) rock salt for first order, with wave-length.—For this simple case, the Darwin-Bragg equation, based on optical theory, reduces to: Reflection coefficient = const. $\times$ $\lambda^3(1+\cos^2 2\theta)/\mu \cos\theta$. Using the experimental values of μ, the theoretical variation with λ is found to be much more rapid than that indicated by experimental data given by various other observers. Possible reasons for this discrepancy are suggested.

ASSUMING the applicability of optical theory to the reflection of x-rays by crystals, Darwin[1] and A. H. Compton[2] some years ago set forth theories expressing the absolute value of the intensity of such reflection as a function of wave-length, angle of reflection, and certain crystal properties. The equations were necessarily complicated, and while in general agreement with preceding and subsequent observations, they have never received a thoroughgoing experimental verification. As these equations have latterly been much quoted in connection with the problem of electronic positions, and as, indeed, they seem to constitute the only presently available means of attacking this problem, it becomes desirable to examine the possibility of experimental checks upon their correctness. It is the purpose of this paper to consider the degree of agreement obtainable between experiment and the theory for a certain important special case of x-ray reflection, viz., first order reflection from (100) planes of rock salt.

The theoretical formula for reflecting power as adapted by Bragg, James, and Bosanquet[3] is stated as follows;

$$\frac{E\omega}{I} = \frac{N^2\lambda^3}{2\mu \sin 2\theta} F^2 \frac{e^4}{m^2c^4} \frac{1+\cos^2 2\theta}{2} e^{-B \sin^2\theta} \qquad (1)$$

[1] Darwin, Phil. Mag., **27**, pp. 315 and 675, 1914

[2] Compton, Phys. Rev. **9**, p. 29, 1917

[3] Bragg, James, and Bosanquet, Phil. Mag. **41**, p. 309, 1921; and **42**, p. 1, 1921

In this equation: $E=$ total energy of wave-length λ reflected by a crystal when rotated once through its reflecting position about an axis in the reflecting plane, with angular velocity ω; $I=$ total energy obtainable per second from the radiation before reflection; $N=$ number of electrons per unit volume of crystal; $\mu=$ effective absorption coefficient of the crystal for radiation of the wave-length λ; $\theta=$ grazing angle of reflection; $F=$ a quantity characteristic of the grouping of the electrons in the atoms of the crystal; $B=$ a function of temperature. The remaining symbols are obvious natural constants.

For the special case here considered certain simplifications may be made. According to Debye,[4] F is a pure function of $\lambda/\sin\theta$, and hence for our purposes remains constant, since the condition for first order reflection is that $\lambda/\sin\theta=2d$. The temperature factor B varies inversely as λ^2, and hence the entire exponential term remains for present purposes constant. Collecting these constants, together with N, e, m, and c, expanding $\sin 2\theta$, and performing a cancellation, we obtain the simplified formula

$$E\omega/I=K\lambda^2(1+\cos^2 2\theta)/\mu\cos\theta. \qquad (2)$$

An obstacle to plotting this equation has been the prevailing uncertainty regarding proper values of the effective absorption coefficient μ. The absorption of rays incident at the angle of reflection is abnormally great in comparison with the usual absorption for the same rays, and this extraordinary absorption does not lend itself to measurement by the simple means used for the ordinary. Bragg, James, and Bosanquet[3] however, have described a means of determining the effective absorption coefficient by a study of transmission reflection as a function of crystal thickness. Reflections by internal planes perpendicular to the faces of a crystal slab vary in intensity with the thickness t of the slab in such a manner that the maximum reflection occurs when $t=\cos\theta/\mu$. By varying the thickness of a reflecting crystal and observing the thickness of greatest reflected intensity, μ may be measured.

Heretofore no determinations by this method have appeared except those of Bragg, James, and Bosanquet, all of which were obtained with the single wave-length .61 A. The following paragraphs present a series of such determinations for a number of wave-lengths and corresponding angles of reflection. All reflections were exclusively of first order and from (100) planes of rock salt. The experimental conditions were briefly the following: Medium focus, tungsten target Coolidge tube, energized from 2 kw transformer supplied by 1 kw motor-generator set, the motor being operated from storage batteries; large Bragg spectrometer with ten inch

[4] Debye, Gött. Nachr. **70**, 1915.

circle and microscopes, carrying 41 cm methyl-iodide chamber with string electrometer rigidly fixed to outer end; tube and chamber slits 28 cm from spectrometer axis with third slit 4 cm in front of crystal; slit adjustments such that with a given chamber setting the maximum wavelength range which might enter the chamber for any rotation of the crystal was about .05 A.

The curves of Fig. 1 show some of the results. The ordinates are electrometer string displacements for one sweep of the crystal through its reflecting position. Movement of the crystal was by a metronome-controlled electrical mechanism. Tube current was constant throughout

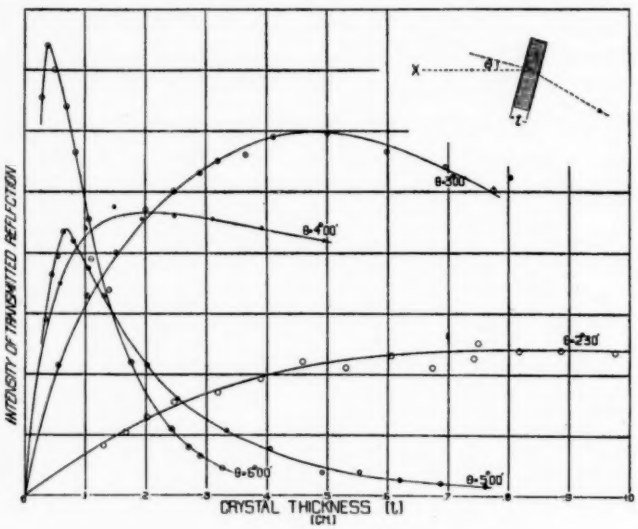

Fig. 1

any one curve, but differed from curve to curve. All observations for any given curve were made with the same crystal, the specimen being ground down slightly between readings. The crystal holder of the spectrometer was devised so that the specimen could be readily removed and as readily dropped into place again in contact with guides against which it was pressed by rubber bands under tension. Grinding was done upon Number 0 emery paper, dry and backed with plate glass. At the beginning of a set of observations each side of the slab was ground until a few tenths of a millimeter had been removed, care being taken to keep the ground faces parallel to the original cleavage. During observations all grinding occurred at one face, the other face serving as a guide to the position of the crystal when placed in the holder. All crystals used were from the same block of rock salt, a fairly clear and uniform specimen seven or eight centimeters in each dimension.

The curves of Fig. 1 are samples from some ten curves actually obtained. The circles of the figure show *all* of the observations made in connection with these five curves. It was not found necessary to throw away any observations, a necessity encountered by Bragg, James, and Bosanquet. This was probably a consequence of using but one crystal for each curve, and indicates that a single crystal of spectrometer dimensions has the same general degree of irregularity throughout.

According to Darwin[5] the procedure described above for obtaining the effective absorption coefficient does not entirely accomplish its end. The abnormally large absorption at reflection angles is explained in terms of an added coefficient known as the extinction coefficient and given by the equation $\mu=\mu_0+\epsilon$, where μ is what we have called the effective absorption coefficient, μ_0 the ordinary absorption coefficient, and ϵ the extinction coefficient. Extinction, in Darwin's words, "may be roughly described as the diminution in the reflected beam due to the fact that when one part of a crystal has reflected some of the radiation, there is less for the parts behind it to reflect." Two types of extinction, primary and secondary, are distinguished, the first relating to the performance of perfect crystals, the second particularly to crystals composed of small perfect fragments imperfectly associated. In general both types of extinction would be expected in a crystal reflection, with the secondary extinction becoming more prominent with increasing irregularity of the specimen. It is to be stated that for rock salt Darwin considers the secondary extinction as far more important than the primary, and Bragg apparently considers it permissible to ignore the primary in computations based upon Eq. (1).

Values of μ were computed from the curves of Fig. 1. The values could not be fitted to an equation of the form $\mu=A\lambda^B$, but the addition of a constant produced the equation

$$\mu=189\,\lambda^{3.9}+.43,$$

which represents the results closely if λ is taken in Angström units, and has been taken as the law of variation of the effective absorption coefficient with wave-length for first order (100) reflections.

It is of interest to examine the behavior of ϵ with varying wave-length. According to the equation in the preceding paragraph ϵ is the difference between the effective absorption coefficient and the ordinary absorption coefficient. The latter was measured for five different wave-lengths in the usual manner, and on subtraction, values of ϵ resulted which could be quite well represented by the equation $\epsilon=195\,\lambda^{4.6}$, which, like the equa-

[5] Darwin, Phil. Mag. **43**, p. 800, 1922

tion for μ, applies only to first order (100) rock salt reflections. It further applies only to secondary extinction but this, as has been said, is thought to comprise by far the greater portion of the total extinction. In view of the proportionality between extinction coefficient and intensity of reflection at constant wave-length, as found by Bragg, James, and Bosanquet, the rapid rise of ϵ with wave-length found here is rather unexpected.

Returning to Eq. (2) the experimental values of μ may be inserted and, assigning an arbitrary value to k, reflecting power may be plotted against wave-length. The lower curve of Fig. 2 is such a plot. This curve may be compared with experimental determinations of first order reflecting

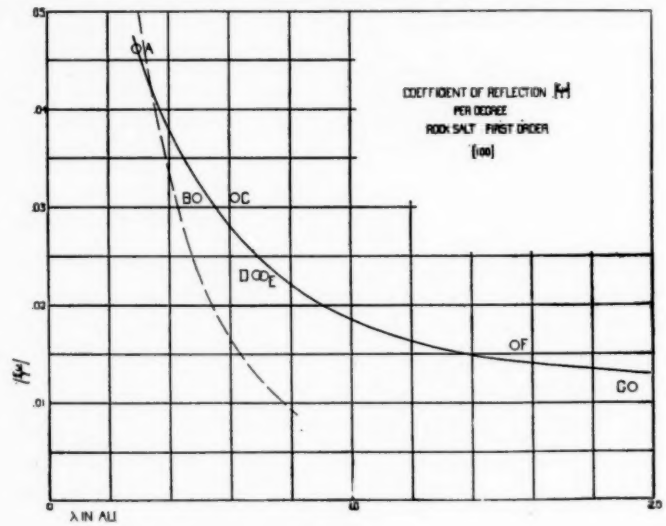

Fig. 2

power. The results of four such investigations are available, including measurements at seven different wave-lengths. The seven points are denoted by the circles lying along the full curve in Fig. 2. Three of these points are by Davis and Stempel,[6] two by Wagner and Kulenkampff,[7] one by Bragg, James, and Bosanquet[3] and one by A. H. Compton.[8]

The discrepancy between these two curves is certainly rather wide. The indications are that (a) the theory of reflection embodied in Eq. (1) is incorrect or incomplete, or (b) the effect of primary extinction even in so imperfect a crystal as rock salt is greater than has sometimes been supposed, or (c) such widely differing degrees of structural imperfection are to be found among rock salt crystals as to make it necessary to meas-

[6] Davis and Stempel, Phys. Rev. **19**, p. 504, 1922
[7] Wagner and Kulenkampff, Ann. der Phys., p. 369, 1922
[8] A. H. Compton, Phys. Rev. **10**, p. 95, 1917

ure $E\omega/I$ and μ with the same specimen if an agreement with theory is to be shown. The last alternative would virtually mean the giving up of these quantities as fundamental physical properties of rock salt and the recognition of them (or at least one of them) as characteristics of particular specimens. The second alternative requires that primary extinction, unlike the secondary, should decrease with increasing wave-length. This view is perhaps supported by the fact, observed by Davis and Stempel, that the reflecting power of calcite changes but little with wave-length compared to the corresponding change with rock salt. Calcite, being the more nearly perfect crystal, should exhibit a greater primary extinction and if primary extinction varies with wave-length in the manner suggested the effect would necessarily be to flatten out the reflectivity curve in the manner found by these investigators.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA,
February 8, 1923.

THE LUMINESCENCE OF TITANIUM OXIDE

By E. L. Nichols

Abstract

Luminescence of titanium oxide.—(1) *Cathode rays* excite only very faintly some orange-red bands unless the oxide has been recently fused, when the light excited has a fine blue color and includes three bands with heads at .625, .550 and .425μ. The fatigue is rapid. (2) *Ultra-violet light* from an iron spark was ineffective. (3) *Under flame excitation*, a sample of the oxide placed on a copper block showed luminescence which was grayish blue at 425°, a strong red to 677° when it suddenly changed to a yellow. (4) *Heated to incandescence* by an oxy-hydrogen flame, two distinct phases were observed. Phase R (hydrogen in excess) showed a reddish luminescence reaching a maximum intensity at about 985° C of about eleven times black body radiation. Phase O (oxygen in excess) showed a modified blue glow greatly in excess of black body radiation throughout all the visible and for all temperatures below 1200° C.

In the Cathode Tube

When the sample[1] of TiO_2 used in the investigations to be described in this paper, was placed in a vacuum tube without previous heat treatment, the only sign of activity was a very faint ruddy fluorescence under bombardment by the cathode-rays. This glow when viewed with a hand spectroscope shows indications of a group of narrow bands in the orange-red but these have not as yet been measured on account of their weakness. So feeble is the luminescence that other samples tested in 1921 were reported as inactive.[2]

When the surface layer of the oxide had been fused in an alundum crucible with the oxy-hydrogen flame impinging upon it from above, the glazed crust formed upon cooling gave a fine *blue fluorescence*, the spectrum of which appeared to consist of three broad overlapping bands with crests at, approximately, .625μ .550μ .475μ (visible to .450μ). The intervening regions in the yellow and green-blue were noticeably dim. Upon standing in the air the fused oxide lost in great measure its power of cathodo-luminescence. Indeed its fatigue within the vacuum tube during bombardment was unusually rapid. Freshly fused samples, during the earlier stages of evacuation, glowed more brightly than at any subsequent time. In its behavior this substance corresponds very closely with the oxides of calcium, silicon, and zirconium.

[1] To the courtesy of Mr. W. L. Lemcke, the writer is indebted for an ample supply of this oxide, which had been prepared by Dr. Rossi.

[2] Nichols and Wilber, Phys. Rev. **17**, 708, 1921

When exposed to the iron spark all samples of TiO_2 which the present writer has had the pleasure of studying, are not luminescent even after heating to incipient fusion. Doubtless like other similar oxides, it could be used as a solvent and would become active when properly blended with other substances such as manganese, chromium or copper.

Behavior under Flame Excitation

When a thin layer of titanium oxide is mounted on the surface of a massive copper block, and is brought into contact with a hydrogen flame, a very feeble, grayish-blue luminescence is discernible within the zone of the flame. If now the copper block be progressively heated, this will be supplanted by a deep red luminescence at a temperature somewhat below the beginnings of incandescence. This grows brighter as the temperature rises and is easily visible superimposed upon the bright incandescence of the copper from which it is distinguishable by its pure red color. At a still higher temperature this luminescence changes to yellow. The maximum of brightness is clearly passed before the temperature of 800° is reached. The glow continues to be visible however almost up to the melting point of copper.

On cooling, the transition from yellow to red is very sudden. It was located at 677°. The red band in its turn disappeared at 425°.

We have then, three distinct out-croppings of luminescence: (1) gray-blue (very feeble), from room temperature to 425° C; (2) red (strong) 425° to 677°; (3) yellow (strong), 677° to about 1,000°.

Studies of the Incandescent Oxide

When instead of heating the oxide by placing a thin layer upon the surface of a copper block and exposing it momentarily to contact with a hydrogen flame, as in the experiments just described under the head of flame excitation, we allow an oxy-hydrogen jet to impinge continuously from above upon a mass of the oxide contained in a crucible, the incandescent material shows luminescence similar to that observed by Ch. Féry[3] in the case of certain other oxides. Here the temperatures are due to the flame and the effects occur between the beginning of incandescence and the melting point of the oxide, whereas in flame excitation the temperatures are controlled by the separately heated block of copper and are only slightly affected by the flame. While the temperatures, in the two methods overlap to a certain extent, the results are quite different and for the most part easily distinguishable. Since the luminescence of incandescent oxides has recently been a sub-

[3] Ch. Féry, Ann. de Chim. et de Phys. (7) **23**, 433, 1902

ject of detailed investigation, the method of observation need not be described further in the present paper.[4]

In the case of TiO_2 the amount of free oxygen present determines the character of the light emitted to an extraordinary degree. In fact at any temperature between the red heat and 1200° the color of a

TABLE I

Luminescence of Titanium Oxide (TiO_2)

	Temp. (black body)	I_{bb} (milli-lamberts)	I_0 (in milli-lamberts) red	green	blue	I_0/I_{bb} red	green	blue
Phase O	692°C	.00275	.0100	.133	.422	3.63	48.3	153.1
	773	.0360	.316	1.58	.537	8.79	43.9	149.3
	882	.634	4.95	14.3	66.8	7.82	22.5	105.5
(Oxygen	970	4.67	14.3	77.6	99.6	3.05	16.6	21.3
in excess)	1044	22.0	66.4	123.6	129.0	3.01	5.62	5.86
	1110	66.3	129.2	191.4	191.0	2.70	3.18	3.18
	1166	167.0	211.0	286.0	286.0	1.27	1.71	1.71
	1219	366.0	432.0	502.0	502.0	1.18	1.37	1.37
	1268	776.0	776.0	776.0	776.0	1.000	1.000	1.000
Phase R	692	.00275	.00183	.00275	.00275	0.668	1.000	1.000
	773	.0360	.0525	.0596	.0596	1.426	1.656	1.656
	882	.634	3.20	2.63	2.63	5.05	4.15	4.15
(Hydrogen	970	4.67	52.5	44.7	44.7	11.2	9.55	9.55
in excess)	1044	22.0	153.0	153.0	153.0	6.96	6.96	6.96
	1110	66.3	180.0	221.0	221.0	2.99	3.67	3.67
	1166	167.0	180.0	180.0	251.0	2.15	2.15	1.51
	1219	366.0	355.0	355.0	417.0	0.971	0.971	1.14
	1268	776.0	776.0	776.0	776.0	1.000	1.000	1.000

mass of the incandescent oxide upon which an oxy-hydrogen jet impinges, may be changed from a deep red to a blue by a very slight adjustment of the gases in the flame.

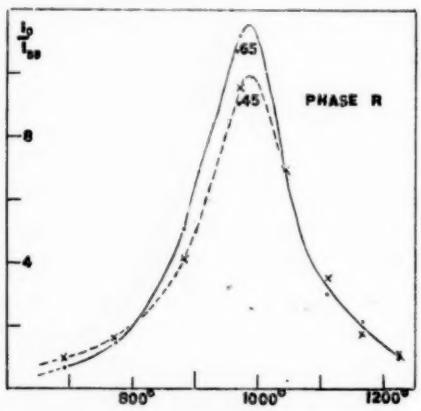

Fig. 1

[4] Nichols and Howes, Phys. Rev. (2) **19**, 300, 1922

We thus have two distinct phases of incandescence, and these have been observed and measured throughout a range of over five hundred degrees. They may be briefly characterized as follows.

Phase R (oxygen meager) is distinguished by an out-cropping of luminescence which reaches a sharply defined maximum just below 1000° and which affects the whole visible spectrum. The red of the spectrum is relatively somewhat stronger at all temperatures between 800° and 1050°. In a measurement made at the crest of the curve the

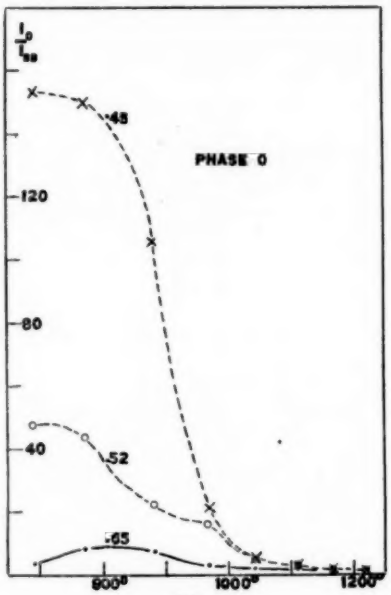

Fig. 2

red (.65μ) was 11.0 times, and the blue (.45μ) 9.8 times as bright as the corresponding regions in the spectrum of a black body at the same temperature.

Phase O (oxygen in excess) is a modified "blue glow." At 700° the brightness in the blue (.45μ) was found to be over 150 times that of the black body, in the green (.52μ) 48 times, and in the red (.65μ) 8 times. The effect differs from the normal "blue glow" of Al_2O_3, BeO, CaO, etc., in that the maximum of relative intensity is within the incandescent range, instead of at some lower temperature, and in that the luminescence extends to the green and red of the spectrum.[5] Above 1200° all excess radiation disappears and the spectrum coincides with that of a black body, both in distribution and brightness. These values appear more definitely in Table I in which the brightness in milli-lamberts

[5] Nichols and Howes, J. Opt. Soc. of Am. **6**, 42 (1921)

of three regions of the spectrum (red, green and blue) are given for both phases of incandescence, and also the ratio I_0/I_{bb} of these intensities to those of the corresponding regions in the spectrum of a black body of the same temperature.

How well defined the outcropping of luminescence is in *Phase R* and how sharp its crest at 985° C, may be seen in Fig. 1.

The modified blue glow which characterizes *Phase O* is illustrated in Fig. 2. The maximum value of I_0/I_{bb} is evidently to be found not far below 700° C. The relative brightness of the green is more than one-

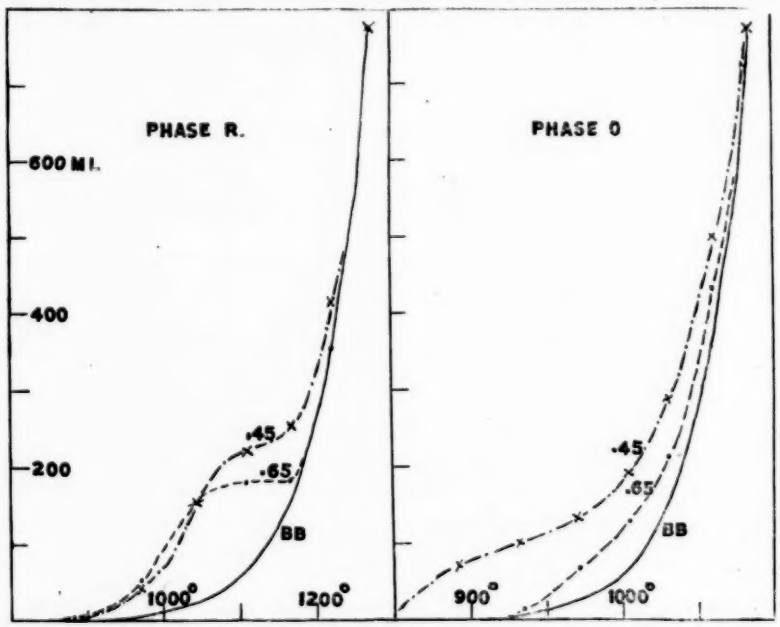

Fig. 3

fourth that of the blue, while the red glows more strongly than the corresponding black body throughout the whole of the range of incandescence. It is for these reasons that the effect in *Phase O* is described as a *modified* blue glow.

These effects may also be depicted as departures from the black body radiation curve (BB) as in Fig. 3. Here the remarkable fact is that the radiation from this oxide throughout the visible spectrum is *in excess* of black body radiation for the whole range of temperatures from the threshold of visibility to 1200° C.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
December, 1922.[6]

[6] Received May 16, 1923

THE PHOTOLUMINESCENCE OF FLAMES

By E. L. Nichols and H. L. Howes

Abstract

Effect of light on the intensity of the flame spectra of Li, Na, Ca, and Sr.— The salted flame of an air-hydrogen blast lamp was illuminated with the full light from a tungsten lamp, a carbon arc, a mercury arc and an iron spark, and the intensity of the bands or lines emitted, as determined by a photometric balance method in connection with a spectrometer, was found to be increased in all cases. The iron spark was most effective, the increases being over 10 per cent for Ca and Sr. Not only the ultra-violet beyond .3μ is effective but also light above .43μ. Red or yellow light of the wave-length absorbed by the flame, however, had a quenching effect, reducing the intensity 2 or 3 per cent and decreasing the effect of the spark alone by half. No change in the distribution of intensity in the spectra seems to be produced, all bands being equally affected. That true luminescence is produced is shown by the fact that the intensity is the same in all directions.

LUMINESCENCE is, at the present time, commonly regarded as a phenomenon of instability, occurring chiefly if not exclusively where matter is dissociating and is entering into new combinations. The conditions within a flame are therefore peculiarly favorable to the production of luminescence and the light from flames containing salts etc., is quite generally ascribed by the chemists to "flame reactions rather than to the direct effect of temperature."[1] Whether the materials within a flame being in a state of rapid dissociation and recombination, are capable of excitation to luminescence by extraneous means appears never to have been considered.

The present writers were led to look for photo-luminescence in flames by discrepancies in some attempted measurements of the opacity of a hydrogen flame rendered luminous by the injection of powdered calcium fluoride. The brightness of the flame plus the light transmitted by the flame from a nitrogen filled tungsten lamp placed behind it should normally be slightly less than the sum of the two intensities taken separately, whereas instead of showing a loss by absorption the *combined brightness was persistently greater*. Various more obvious explanations having been disposed of we were driven to the conclusion that the flame was actually somewhat brighter when exposed to the light of the neighboring source.

[1] For a very complete discussion see Bancroft and Weiser, J. Phys. Chem.; **18**, pp. 118, 213, 762, (1914); **19**, p. 310, (1915).

The experiments which followed this entirely unanticipated result will be described briefly in this paper.

The Method

In the observation of the flames under consideration, all of which had bright banded spectra of the familiar type obtained when salts of Li, Na, etc., are introduced into a nonluminous flame, it was advantageous and convenient to deal with a single band instead of with the flame as a whole. For this purpose a Hilger constant deviation spectrophotometer was used, the collimator slits of which were maintained at constant width. As in various investigations already described, intensities of the contrast field were balanced by moving the comparison light T, Fig. 1, a small nitrogen filled tungsten lamp maintained on a storage battery circuit, along a photometer bar in front of the slit C_2. The flame F was directly before the other slit C_1.

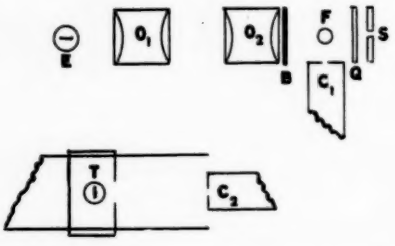

Fig. 1. Diagram showing arrangement of apparatus.

The flame in most of our experiments was a hydrogen flame from an ordinary blast lamp. The salt which rendered it luminous was introduced with the air supply either in the form of a dry powder or of spray. In the former case the blast of air entered a short glass tube T, Fig. 2 A, through a narrow vent bent downward so as to stir up the surrounding powder and carry a portion into the flame.

This method afforded a very bright flame when dry powders were obtainable, $CaFl_2$, SrS, NaCl, etc., but the steadiness was inferior to that of flames supplied with a sprayed solution. In later measurements therefore the aspirator described by Bancroft and Weiser[1] was used. It consisted of an Argand chimney B, Fig. 2, closed at both ends, with the usual double tube with contracted tips inserted through the base. The outlet above was shielded by a suspended crucible cover C.

Having established the fact that the increase in brightness of the hydrogen flame was practically independent of the direction from which it was illuminated, which was quite what one would expect in the case of luminescence, we mounted a pair of lantern objectives of large aperture, O_1 and O_2 Fig. 1, with their common axis at right angles to that of the collimator. The exciting source E was placed at the principal

focus of O_1 and its image fell within or sometimes just beyond the flame so that the pencil of rays passed through that part of the flame which was in line with the collimator. A swinging shutter B, which could be moved by the observer at the eyepiece of the spectrophotometer, served to admit or exclude the exciting light.

While it is a simple matter to detect with certainty variations of the order of five per cent due to light added to or subtracted from an otherwise steady source of light, to do so in case of a rapidly and irregularly fluctuating flame is not a matter of mere inspection. The increment due to exposure is immediately submerged in the natural drift, and the only satisfactory method is to make a considerable number of settings rapidly, and at nearly regular intervals of, say, thirty seconds with the flame alternately exposed and unexposed. Two observers, of whom one opens and closes the shutter and reads the photometer bar while the other sets the comparison lamp promptly upon signal, never readjusting his setting and ignoring so far as possible the position of the shutter, can obtain very consistent results in this way. If the readings thus made are plotted as though the time intervals were constant, which strictly speaking they are not, an immediate indication is had of the character and approximate size of the effect. Numerical values may then be obtained by averaging over the ranges within which disturbances are least troublesome. Effects too small to be detected by the observer at the eyepiece, because of the drift, are thus brought out with certainty. Figs. 3 and 4 will serve to elucidate this procedure.

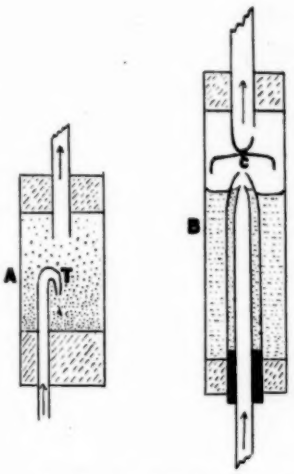

Fig. 2. Devices for introducing salts into flame; A in powder form; B in solution.

THE RESULTS

Of the various exciting sources employed, including the tungsten lamp, the carbon arc, the mercury arc and an iron spark, the spark was relatively the most effective. From this it was clear that the *enhancement of the bright bands of these flame spectra is produced by radiation of the shorter wave-lengths*. Moreover since the effect was greatly reduced (e. g. from 5.9 to 3.6 per cent in an experiment with the lithium flame) by inserting a glass plate instead of quartz between the spark and flame there was obviously considerable excitation by wave-lengths for which glass is

opaque. On the other hand we obtained marked excitation through a deep purple glass which aside from the usual cobalt band in the red, was opaque to all wave-lengths up to .43μ. The near ultra-violet was thus indicated as an active region.

Measurements with various light filters interposed between the flame and the exciting source, a tungsten filament, revealed further the existence of a *quenching effect of the longer wave-lengths* of the visible spectrum analogous to the action of infra-red rays upon the phosphorescent sulphides. A sodium flame upon which the image of the glowing filament

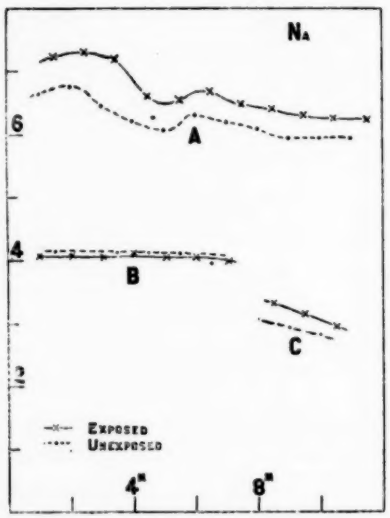

Fig. 3. Observations with Na flame.

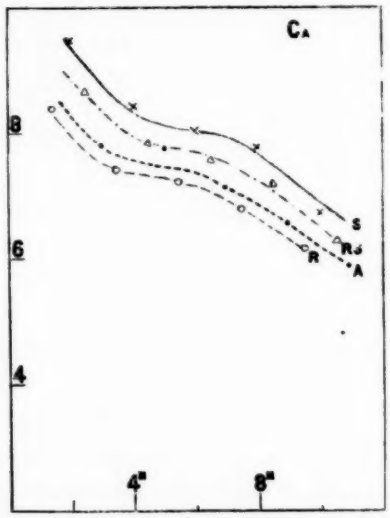

Fig. 4. Observations with Ca flame.

was focused was increased in brightness by exposure as shown in Fig. 3 A, in which readings with and without excitation were made alternately. The average effect for this run was +6.0 per cent. A repetition with a deep amber glass interposed gave the result shown in Fig. 3 B where the effect of illumination, although very slight, was distinctively negative (−1.2 per cent). Upon removing the screen (Fig. 3 C) the conditions indicated in Fig. 3 A recurred.

Quenching is still better exhibited by an experiment in which the hydrogen flame was supplied with spray containing $CaCl_2$. Excitation was by an iron spark S, Fig. 1, placed about 5 cm from the flame, with a quartz window interposed. The flame could likewise be exposed at will to a red light from the tungsten filament by means of a dense ruby glass placed between the lenses O_1 and O_2, Fig. 1.

Calcium band at λ .6475μ. Observations were made upon the red band of the calcium flame at .6475μ, a wave-length which was *included*

within the band transmitted by the ruby glass. This was a coincidence favorable to test the analogy to the quenching of the phosphorescence of the sulphides, since, as is well known, the only active rays in that case are those corresponding in wave-length to an absorption band of the substance.

The procedure in the present experiment was to measure successively the brightness of the band with the flame (1) unexposed, (2) exposed to red, (3) excited by the spark, (4) excited by the spark and also exposed to red. This cycle was repeated several times with results which are indicated graphically in Fig. 4, where curves A, R, S, and RS give the brightness of the band in the four successive steps, respectively.

From these curves it will be seen that enhancement by illumination (compare curves A and S) is about 11 per cent; the quenching effect (compare curves A and R) is likewise unmistakable, and equal to about two per cent; and the combined effort of the spark and the red light is an enhancement of about 5 per cent.

From this it appears that while the red light reduces the brightness of the observed band in the spectrum of the unexposed flame by only two per cent, it cuts down the effect of the spark upon the flame to one-half of its normal value. In other words *the quenching by red light affects chiefly, perhaps wholly, the photo-excited luminescence of the flame.*

To explain the effect of the red light upon the unexposed flame, we may suppose that although visible radiation in so far as it is due to mechanisms other than those put into motion by the exciting light, is not subject to quenching, a certain amount of auto-excitation exists, the materials capable of photoluminescence being affected by the violet and ultra-violet radiation within the flame itself.

Strontium band λ .655μ. Measurements similar to those just described were made upon the red band λ .655μ of a strontium flame, i. e., of a hydrogen flame supplied with a spray of $SrCl_2$. The average results for the increase of brightness are: (1) effect of spark excitation +9.7 per cent; (2) effect of exposure to red −2.6 per cent; combined effect of spark and red +5.7 per cent.

Lithium line λ .6708 μ. In some observations upon the red line, λ .6708μ, of a lithium flame advantage was taken of the fact that the transmission band for red of a sheet of cobalt glass included the wave-length of the lithium line. The exciting light from a tungsten filament was passed through this glass before being focused upon the flame. The red light from the exciting source could be cut out by interposing as a second filter a cell containing a suitable solution of ammonio-sulphate of copper. Readings upon the brightness of the lithium line

made alternately through the cobalt glass alone and through both filters, showed increased intensities when the red light was removed. Without correcting for the diminished strength of excitation due to absorption by the second filter, this increment exceeded thirty per cent of the total photoluminescence. Similarly it was found that the exciting power of a source, such as the carbon arc, was measurably increased by the interposition of a screen opaque to the longer wave-lengths of the visible spectrum.

Sodium lines. Experiments on quenching of the sodium flame with red light gave a negative result; the average intensity of the yellow lines being the same, when exposed as when unexposed, to within .2 per cent, or in other words to well within the errors of setting. When, however an amber glass screen was used as described in our earlier paragraph instead of the ruby glass, quenching occurred to an extent easily measurable. In the former case there was presumably but little absorption by the luminescent material; in the latter there would be complete absorption in the region of the lines of sodium at 6154 and 6160.

Effects similar to those obtained by the use of light filters in the foregoing experiments were likewise produced by focusing the spectrum of a linear filament in the vertical plane through the extension of the axis of the collimator *C* and exposing the flame under investigation to different portions of the spectrum.

In these tests, in which Mr. T. Tanaka, a practiced experimenter with the spectrophotometer, kindly acted as observer at the eye-piece, excitation was obtained with the shorter wave-lengths, and this was changed to quenching when the flame was exposed to red. The results with these necessarily feebler illuminations, were not of a size to warrant an attempt to work out the effect, wave-length by wave-length, with monochromatic light.

Relative effects on different bands of the same spectrum. Thus far effects on a single band only have been described. Measurements of several of the brighter bands in the flame spectrum of calcium and strontium indicated, however, that under a given excitation there was enhancement of all the bands in approximately the same proportion, whether the band was in the red, orange or green. Under the action of the inhibiting rays, it was found likewise that quenching was not confined to the band lying within the region of the light transmitted by the filter, *but was equally apparent in bands lying beyond that zone.* It is therefore concluded that the emission spectrum of a flame is to be regarded as a unit. *When*

it is excited to luminescence all its bands are enhanced, and when it is exposed to quenching by absorbed light all its bands are quenched.

Variations in flame sensitiveness. Early in the course of the experiments described in this paper it was noticed that the sensitiveness of flames to photo-excitation differed greatly. The flame of the Bunsen burner, for example, was found to be almost entirely unaffected. The upper portion of the hydrogen flame with admixture of air, as used by us, was more sensitive than the base. A set of measurements on the sodium flame to determine this difference, gave for a region near the tip 7.4 per cent and for one near the base 5.5 per cent, the exciting source being the same in both cases.

Fluctuations in sensitiveness produced by slight adjustments of the air blast suggested a dependence upon the supply of free oxygen and this was tested by enriching the surrounding atmosphere with this gas. In this way a rather insensitive calcium flame was increased in sensitiveness from 4.3 per cent to 9.1 per cent for a given illumination.

Relation of photoluminescence to flame contents and flame reaction. In the class of flames upon which the observations described in this paper were made, certain chemical constituents are present and certain flame reactions occur. For a hydrogen flame into which calcium chloride has been introduced, for example, we shall have among other substances, Ca and Cl (in both atomic and ionized form); also CaO. In such a flame there must be continually going on the dissociations and recombinations commonly accompanying the phenomenon of luminescence. Since no new bands are introduced by photo-excitation it seems reasonable to suppose that the vibrating mechanism which produce the flame spectrum are the ones excited to additional activity by light.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
December, 1922.[2]

[2] Received May 16, 1923

MOBILITIES OF ELECTRONS IN GASES

By K. T. Compton

Abstract

Motion of electrons through gases.—The theoretical equation for mobility constant obtained in a recent paper, is put in the form

$$K=2.54(10^3)l_0\left\{1+[1+1.355(10^6)Ml_0^2(E/p)^2]^{\frac{1}{2}}\right\}^{-\frac{1}{2}}$$

where l_0 is electronic mean free path at 1 mm pressure, M is molecular weight relative to H, E is the electrical field in volts/cm, and p is pressure in mm Hg; and it is tested by comparison with recent experimental data obtained by Loeb and by Townsend and co-workers. Although the equation contains no arbitrary constant if l_0 is taken from kinetic theory, the agreement with experiments is good in the case of H_2 and within a small factor in the case of He, N_2 and A, for values of E/p less than the critical value which is characteristic of each gas and equal to about 20 for H_2, 1.3 for N_2, 0.5 for A, and $>.4$ for He. *Elasticity of collisions.* In explanation it is suggested that when electrons collide at speeds greater than the critical for the gas, the collisions are no longer perfectly elastic, as assumed by the theory. In the region of elastic collisions, the equation may be used to compute the actual equivalent *mean free paths* for elastic spheres from the measured values of K, for comparison with the kinetic theory values of l_0. This free path in H_2 is close to the kinetic theory value, in He it is a little less, while in N_2 and A it is greater and varies with the speed, being greater at small speeds. These free paths are compared with values determined in other ways and the differences are attributed to differences in the meaning attached to the term collision. The data for O_2 and CO_2 are insufficient to give the values of the critical E/p but indicate that these are lower than for the other gases.

IN a preceding paper[1] the nature of the motions of electrons in gases in an electric field was considered with reference to the energy lost at collisions, the terminal speed acquired, the number of collisions made and the average rate of drift in the direction of the field. Particular attention was given to the special case in which collisions between electrons and molecules are treated as if between elastic spheres. The purpose of the present paper is to compare the consequences of this theory with results of experimental determinations of electron mobilities in gases.

Owing to the large values of the mobility and complicating results of temporary attachments to gas molecules, it is only recently that these mobilities have been measured with any claim to accuracy. Loeb[2, 3] has successfully applied a modification of Rutherford's[4] alternating current

[1] Compton, Phys. Rev. **22**, 1923
[2] Loeb, Phys. Rev. **19**, 24, 1922
[3] Loeb, Phys. Rev. **20**, 397, 1922
[4] Rutherford, Proc. Camb. Phil. Soc. **9**, 401, 1898

method and Townsend[5,6] has developed a new method depending on the deflection of the direction of average drift by a transverse uniform magnetic field. Loeb's method is the more direct, but is subject to uncertain corrections due to a.c. wave form, persistence of ions between cycles and lag of terminal speed behind impressed e.m.f., from which Townsend's method is free.

The equation for the electron mobility derived in the preceding paper is

$$\mu = \frac{0.815el}{\sqrt{m}[\alpha T + (\alpha^2 T^2 + l^2 M E^2 e^2/1.134m)^{\frac{1}{2}}]^{\frac{1}{2}}}, \tag{1}$$

in which e and l are the electronic charge and mean free path, m and M are the masses of electron and molecule, αT is the mean energy of thermal agitation of gas molecules, and E is the electric intensity. This equation may be considered as a corrected form of an equation recently proposed by Loeb.[3] All mobilities considered in this paper are reduced to standard conditions, being expressed as mobility constants K, given by

$$K = (p/760)(273/T)\mu. \tag{2}$$

Since the mean free path l varies inversely as the pressure, we may put $l = l_0/p$, where l_0 is the mean free path at 1 mm pressure. We thus see that K is a function of E/p, which takes the following form when numerical values are substituted for certain constants:

$$K = \frac{254000 l_0}{[1 + (1 + 1355000 M l_0^2 (E/p)^2)^{\frac{1}{2}}]^{\frac{1}{2}}}, \tag{3}$$

in which E is expressed in volts per cm and M is the molecular weight on the basis $M_H = 1$.

Hydrogen

Fig. 1 shows the experimental data and the theoretical curve (1) obtained by substituting $M = 2$ and $l_0 = 0.0784$ cm in Eq. (3). This is the kinetic theory value of l_0 given by $l_0 = 4\sqrt{2}L_0$, where L_0 is the molecular mean free path at 1 mm pressure. Townsend and Bailey's[6] values fall nearer the theoretical curve than do Loeb's.[7] When it is noted that Eq. (3) contains no adjustable constants, the agreement is rather striking. If the electronic mean free path were 0.58 of the kinetic theory value, Eq. (3) would give curve (2) which falls fairly well through the mean of Loeb's values of K. The failure of all of Loeb's data, taken at different

[5] Townsend and Tizard, Proc. Roy. Soc. **88**A, 336, 1913

[6] Townsend and Bailey, Phil. Mag. **42**, 873, 1921

[7] In this connection it may be remarked that Loeb's results have all been corrected slightly for a.c. wave form by a factor which has not yet been published, but which Dr. Loeb kindly communicated to me.

pressures, to be expressed as a single function of E/p suggests that some one of the corrections noted above should be applied to them.

Nitrogen

Fig. 2 presents Loeb's data on nitrogen and one determination by Townsend and Bailey.[6] Curve (1) is the theoretical curve of Eq. (1), taking the kinetic theory value of $l_0 = 0.0405$ cm. The actual values of K are considerably larger than the predicted values.

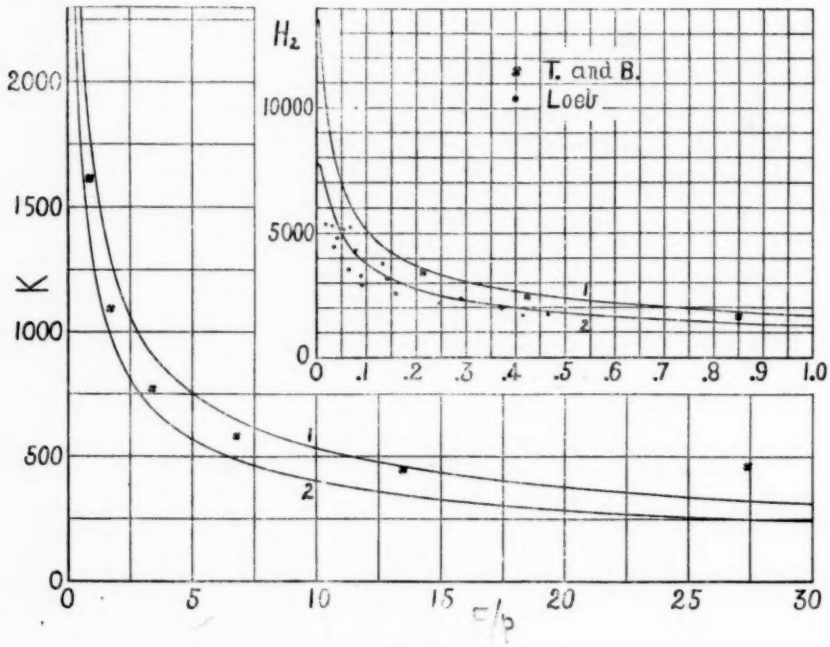

Fig. 1

There are two ways, indicated by the theory, whereby abnormally large values of K may be accounted for. (1) The electronic mean free path l_0 may be larger than the value predicted by kinetic theory, as is not unreasonable since the phenomenon of electron impact may be quite different from that of molecular impact. (2) The electron impacts may result in a greater loss of energy than that characteristic of perfect elasticity assumed in Eq. (3). It is shown in the previous paper that the effect of a *small* departure from perfect elasticity is to decrease the last term in the denominator of equation (3), whereas *large* departures from perfect elasticity lead to values of K which, in the limiting case of complete energy loss at impacts, are given by

$$K_i = 7.01(10)^4 \sqrt{(l_0 p/E)}. \qquad (4)$$

Which of these two variations from the conditions assumed in Eq. (3) is responsible for the large values of K in nitrogen may be inferred by examining the shape of the theoretical curves on the two hypotheses. Increasing the value of l_0 increases K relatively more for small values of E/p than for large ones, thus leading to a steeper curve. This is illustrated by curve (4) which is calculated on the assumption of a free path l_0 four times the kinetic theory value. On the other hand, an increase in the energy loss at impacts tends to flatten the curve, increasing

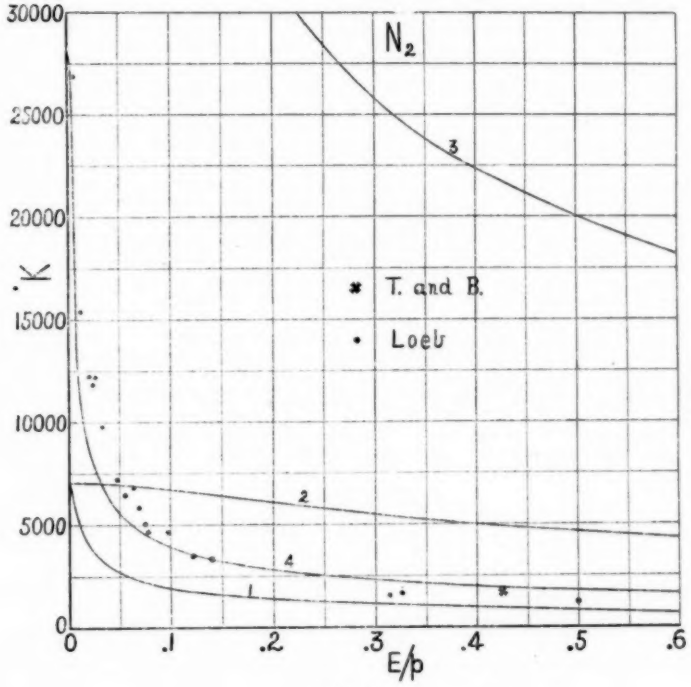

Fig. 2

K relatively more for large values of E/p. This is shown by curve (2), which is calculated on the assumption that the electrons lose on the average 0.05 of their energy at a collision, instead of the fraction 0.000038 characteristic of perfect elasticity.[8] If the impacts were completely inelastic, the electrons not even retaining their thermal energy of agitation after impacts, the mobility constant would be given by curve (3) from Eq. (4). It is evident that the assumption of an abnormally long mean free path gives best agreement with experiment. To secure perfect agreement, however, it is necessary to assume that the free path varies somewhat with the speed, being longer at the smaller speeds.

[8] Compton, loc. cit.[1]

Fig. 3 shows values of K determined by Townsend and Bailey for larger values of E/p, and curves (1) and (4) extended from

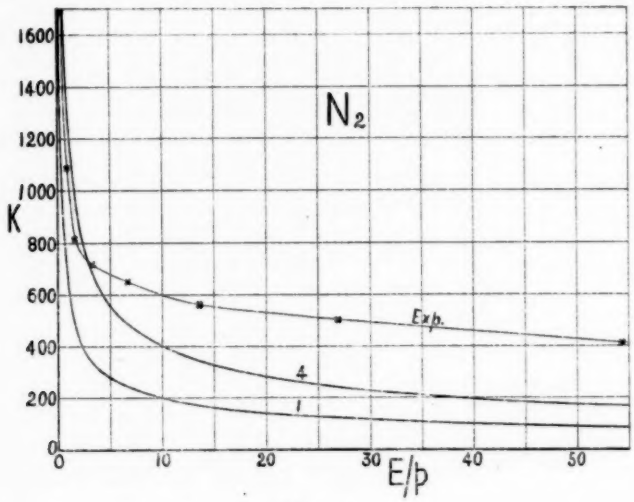

Fig. 3

Fig. 2. There is a notable increase of K above the theoretical values at large values of E/p. This increase is noted also in hydrogen and espe-

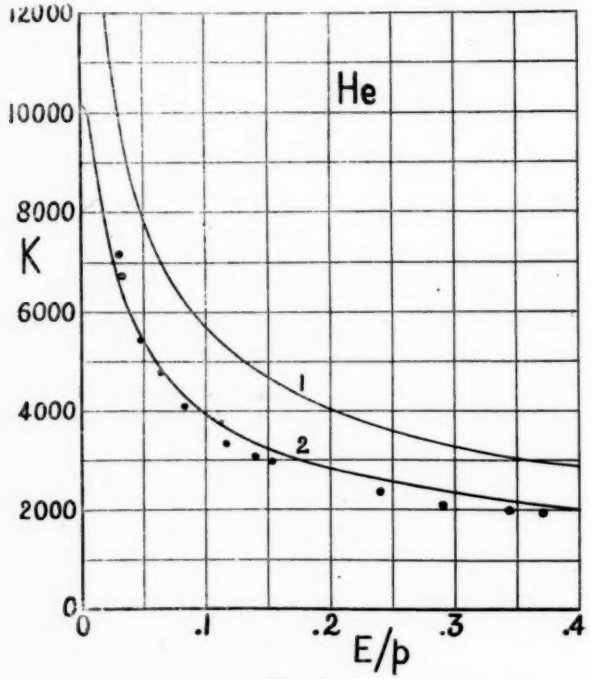

Fig. 4

cially in argon and carbon dioxide, and is evidently due to the setting in of inelastic impacts at the larger values of E/p. This is discussed later in the paper.

Helium

The only available data are those of a preliminary nature kindly communicated to me by Dr. Loeb. If they are in error it is probable that they are too large, since it was found that K was increased by the presence of impurities. Curve (1) represents Eq. (3) using the kinetic theory value $l_0=0.1223$ cm and curve (2), which fits the data well, is calculated on the assumption that $l_0=0.5$ of the kinetic theory value.

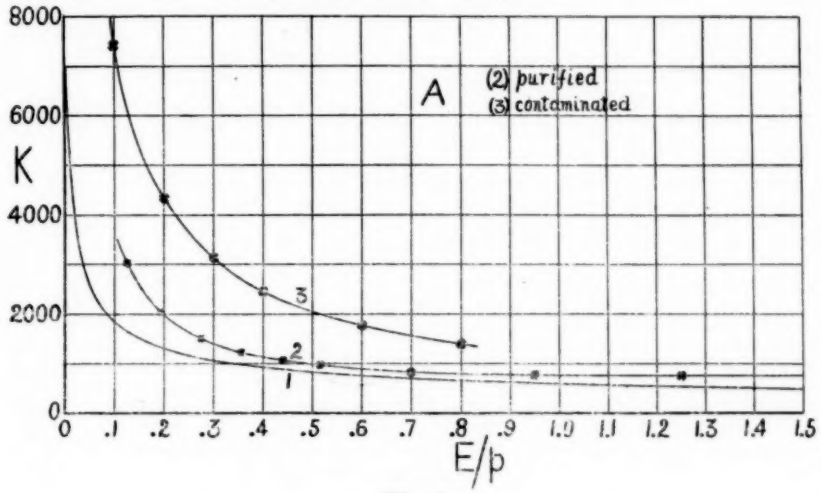

Fig. 5

Argon

Curve (1), Figs. 5 and 6, represents the theoretical K for argon, using the kinetic theory value of $l_0=0.043$ cm. Curve (3) gives the early experimental results of Townsend and Bailey,[9] and curve (2) shows their later results with argon more carefully purified.[10] The indication is that in argon the mean free path is larger than the kinetic theory value. The effect of inelastic impacts beyond $E/p=1$ is especially prominent.

Oxygen

Eq. (3) with $l_0=0.0428$ cm gives curves (1), Fig. 7, whereas Townsend and Bailey's[6] results lie on curve (2). The shape of this curve suggests that the large values of K are, in this case, due to imperfect elasticity of impacts rather than to abnormally long free paths.

[9] Townsend and Bailey, Phil. Mag. **43**, 593, 1922
[10] Townsend and Bailey, Phil. Mag. **44**, 1033, 1922

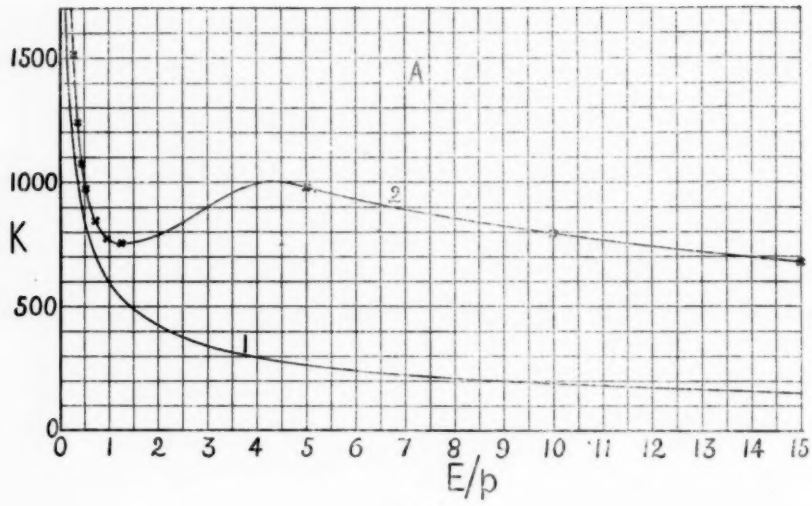

Fig. 6

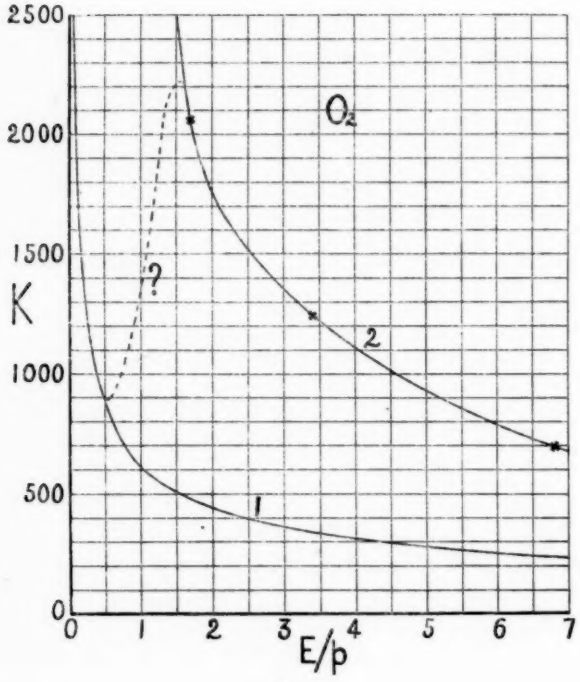

Fig. 7

CARBON DIOXIDE

Eq. (3), with the kinetic theory value of $l_0 = 0.0272$ cm, gives curve (1), Fig. 8, while the experimental values obtained from the work of

Skinner[11] are shown on curve (2). Here there is evidence that inelastic collisions set in at much smaller values of E/p than in the other gases except possibly oxygen. Apparently collisions are elastic up to some value of E/p below 0.3. The upper portion of the experimental curve probably corresponds to curve (2) for oxygen, suggesting that experiments in oxygen with lower values of E/p would show lower values of K characteristic of elastic impacts.

We conclude, in agreement with other lines of evidence, that electron impacts are generally less elastic in CO_2 than in the other gases, except possibly oxygen, but we must interpret this as meaning simply that

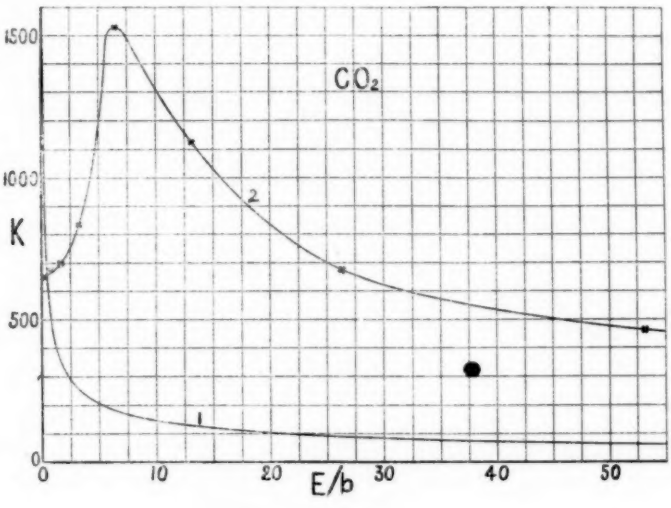

Fig. 8

inelastic impacts set in at smaller energies of impact. Rough calculations, based on methods discussed in the next section, indicate a minimum energy for inelastic impact not greater than one tenth the value in the other gases.

Free Paths of Electrons

There is evidently some reason to accept the general correctness of Eq. (3) for the preceding gases in the range of values E/p below which there is no evidence of inelastic impacts. If we assume its correctness, we may use it to compute the values of the electronic mean free path l_0 at 1mm pressure, and the way in which this free path varies with the speed of the electrons. Solving Eq. (3) for l_0 gives

$$l_0 = 5.38K^2[1.236(10)^{-12}/K^2 + 0.159(10)^{-16}M(E/p)^2]^{\frac{1}{2}}. \quad (5)$$

[11] Skinner, Phil. Mag. **44**, 994, 1922

Substitution of experimental values of K leads to values of l_0 given in Table I.

The value of mean energy U is calculated by Eq. (12) of the preceding paper.

TABLE I

l_0 = electronic m. f. p. at 1 mm pressure;
l_K = value of l_0 predicted by kinetic theory;
l_T = value calculated by Townsend;
U = average kinetic energy of electrons, in equivalent volts.

Data	Gas	E/p	U (volts)	l_0 (cm)	l_0/l_K	l_T (cm)
Loeb	H_2	0 to 0.5	0.0372 to 0.249	0.0452 approx.	0.577	
T. & B.	H_2	0 to 15	0.0372 to 6.90	0.0784	1.000	0.036 to 0.028
Loeb	N_2	0.05	0.109	0.296	7.30	
		0.1		0.201	4.96	
		0.2	to	0.132	3.26	
		0.3		0.099	2.44	
		0.4		0.090	2.21	
		0.5	0.907	0.082	2.02	
T. & B.	N_2	0.425	1.30	0.137	3.38	0.038
		0.850	2.15	0.114	2.82	0.033
Loeb	He	0 to 0.4	0.0372 to 0.222	0.0611 approx.	0.50	
T. & B. (2)	A	0.0	0.0372			
		0.1	0.599	0.222	5.16	0.22
		0.2	0.591	0.109	2.54	0.147
		0.3	0.683	0.084	1.97	0.110
		0.5	0.902	0.068	1.57	0.091
*		0.7	1.120	0.062	1.4	0.085
*		1.0	1.478	0.056	1.3	0.086

*Extrapolated values of K into region where K is affected by inelastic impacts

These values of l_0 do not agree very well with directly determined values recently published by Mayer[12] and by Ramsauer.[13] Their "specific absorbing powers," converted into terms of l_0, give the following average results:

Gas:	H_2	N_2	He	A($U=0.7$)	A($U=1.2$)
l_0	0.022	0.031	0.053	0.227	0.132
l_K:	0.078	0.041	0.122	0.043	0.043

l_K is the kinetic theory value in each case, included for comparison. It should be said that the value of l_0 will depend somewhat on the

[12] Mayer, Ann. der Phys. **64**, 451, 1921
[13] Ramsauer, Ann. der Phys. **64**, 513, 1921

definition of a collision. Certainly Mayer's experimental method, and probably also Ramsauer's, do not measure exactly the same quantity as enters into Eq. (3) and they involve different speeds at impact. The experimental results of Akesson[14] on nitrogen agree much better with Table I, but there is some question regarding their correct interpretation.[15]

Townsend's values l_T and those calculated by Eq. (5) agree fairly well in the case of argon, and also in other cases the agreement is better than with the values of Mayer and Ramsauer. Townsend's l_T has more nearly the same significance as the l_0 used in the present paper. His values should be nearer the true values, since his method depends less on assumptions regarding the nature of impact than do those calculated by Eq. (5).

In this connection it should be recalled that we have, for simplicity, treated collisions as if between elastic spheres. This puts a definite interpretation on the meaning of l_0, and also justifies a neglect of the correction due to "persistence of velocities" at impacts. Recently H. A. Wilson[16] has shown that, if the molecule be considered as a positive core surrounded by a sperical shell of negative electricity, the correction for persistence of velocities takes an interesting form, being less than unity in a certain range and greater than unity elsewhere. Possibly this correction may account for at least part of the variation in l_0 shown in Table I. Our value of l_0 should therefore be defined as the "equivalent mean free path for elastic spheres," and will depart from the true value of l_0 for any gas to an extent depending on the degree to which this conception of an impact is in error.

Effect of Inelastic Impacts

An examination of the values of the kinetic energy U of the electrons in Table I shows that the increase in K observed in the figures at large values of E/p begins when E/p is large enough to give such a mean energy U that an appreciable number of electrons have energies exceeding the critical value above which inelastic impacts may occur. This critical energy is lower in carbon dioxide and probably also in oxygen than in the other gases. An approximate estimate of the effect of these inelastic impacts on the resulting mobility may be made as follows.

Out of N electrons, let F represent the fraction which have speeds greater than V_0, which is the critical speed above which impacts with

[14] Akesson, Lunds Univ. Archs. **12**, no. 11
[15] Cf. Mayer[12]
[16] Wilson, Proc. Roy Soc. **103** A, 53, 1923

molecules may be inelastic. If this fraction is small, we may neglect the influence of inelastic collisions of this group in reducing the average speed of all the electrons, and consider the remaining electrons to have the same average speed as if no inelastic impacts occurred. We may then consider the total current $Ne\mu E$ as due to the sum of the currents carried by the two groups, NF electrons making inelastic impacts, and moving with mobility μ_i and $N(1-F)$ electrons making elastic impacts and moving with mobility μ_e. Actually, of course, these groups do not remain distinct, but statistically they may be treated separately provided F is small. Thus

$$Ne\mu E = NeEF\mu_i + NeE(1-F)\mu_e.$$

In terms of mobility constants, this is equivalent to

$$K = FK_i + (1-F)K_e. \tag{6}$$

K_i is given by Eq. (4) and K_e by Eq. (3). In most cases inelastic impacts set in at energies considerably greater than the mean energy of thermal agitation, so that for the present purpose the terms αT of Eq. (1) may be neglected and Eq. (3) used in the form

$$K_e = 7440\sqrt{\frac{l_0}{\sqrt{M}} \cdot \frac{p}{E}}. \tag{7}$$

The fraction F is obtained from Maxwell's distribution equation as

$$F = 4\pi\left(\frac{h}{\pi}\right)^{3/2} \int_{v_0}^{\infty} v^2 \epsilon^{-hv^2} dv,$$

where $h = 3/(2c^2)$ and c^2 is the mean square speed. Since v_0 is in general much larger than c, we may integrate in series, thus obtaining

$$F = \sqrt{\frac{6}{\pi}} \cdot \frac{v_0}{c} \epsilon^{-(3/2)(v_0^2/c^2)} \left(1 + \frac{c^2}{3\,v_0^2} - \frac{c^4}{9\,v_0^4} + \frac{c^6}{9\,v_0^6} - \frac{5c^8}{27\,v_0^8} + \cdots\right) \tag{8}$$

Similarly, since the energy of thermal agitation is negligible, we may express the mean terminal speed by Eq. (15) of the preceding paper, recalling that the mean speed $\bar{v} = 0.922c$, and reducing to

$$c = 2.68(10)^8 \ (\sqrt{M} \cdot l_0 E/p)^{\frac{1}{2}} \text{ cm/sec.}, \tag{9}$$

where E is in volts per cm and M is on the basis of 1 for hydrogen. In terms of equivalent volts, the mean terminal energy is

$$U = 20.2\ l_0\ \sqrt{M} \cdot E/p. \tag{10}$$

We now write Eq. (6) in the form

$$K = K_e + (K_i - K_e)F = \sqrt{(l_0 E/p)}[7440/M^{\frac{1}{2}} + (70100 - 7440/M^{\frac{1}{2}})F]. \tag{11}$$

We may thus calculate K for any gas by substituting the molecular weight M and the value E/p in Eq. (11), evaluating F by Eq. (8), in

which the ratio $c^2/v_0^2 = U/V_0$, where U is given by Eq. (10) and V_0 is the minimum potential of inelastic impact.

The following table shows, as examples, the effect of applying Eq. (11) to hydrogen and argon, the effect of inelastic impacts being expressed by $\Delta K/K$, which is the fraction by which the mobility constant is increased as a result of inelastic impacts. The equation predicts effects due to inelastic impacts at about the right values of E/p, the discrepancies

	Hydrogen			Argon		
E/p	0.5	1	2	0.25	0.5	1
$\Delta K/K$	.000054	.032	.73	.003	.23	2.73

being in the nature of predicting too large an effect rather than too little. This is not surprising since Eq. (11) involves the most favorable assumptions, such as an inelastic impact at *every* collision with speed above v_0 and an impact so inelastic that not even thermal energy of agitation is retained. It is therefore to be expected that Eq. (11) should overestimate the increase of mobility due to inelastic impacts. It is quite likely that these inelastic impacts do not result in complete loss of energy, but only of an amount equal to eV_0, any excess of energy being retained as energy of agitation of the electrons. In view of the uncertainties involved it does not seem worth while to attempt a more precise treatment at present. It is sufficient to have shown that inelastic impacts are the probable cause of the increase in K at large values of E/p. Eq. (3) is applicable only at smaller values of E/p.

Conclusions

The general results of this study may be summarized as follows. The support of the theoretical mobility equation is sufficiently good to give confidence in the approximate correctness of equations for terminal speed, number of collisions while advancing unit distance, etc., which were deduced in the preceding paper. The departures of the theory from experimental results suggest the ways in which electron impacts in various gases and at various speeds differ from impacts between elastic spheres. The mean free path employed in the theory may be looked upon as the "equivalent mean free path of elastic spheres." Its value is determined by Eq. (5) from actual values of the mobility constant K. If these "equivalent values" are used instead of the kinetic values of l_0 in the equations of the preceding paper, these equations should be quite accurate in the case of those gases in which impacts are elastic.

In this connection it is interesting to note the strong evidence that slow speed electrons make nearly or perfectly elastic impacts with the multiatomic molecules. This is in agreement with the observations

of Foote and Mohler and their collaborators, who found just as strong evidence for elastic impacts in these gases as in monatomic gases. It appears that the older view that electrons make quite inelastic impacts in multiatomic gases, must be replaced by the view that impacts in most or all such gases are quite elastic provided the energy is less than that required, according to the quantum relation, to produce radiation or dissociation in the gas.

We must then look to another explanation of the different behaviors of monatomic and multiatomic gases as regards ionization and arc characteristics. Evidence is accumulating to show that this difference is due to the production of resonance radiation with resulting high concentration of excited atoms because of the strong absorption of this radiation by the gas. In multiatomic gases the result of inelastic impacts is either dissociation or the excitation of elements of band spectrum, which are not strongly absorbed by the gas and do not, therefore, tend so much to facilitate ionization of the gas.

In my conclusion, I wish to express my indebtedness to Dr. Loeb for placing data at my disposal and for suggestions and criticisms.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
May 19, 1923.

POTENTIAL DISTRIBUTION BETWEEN PARALLEL PLANE ELECTRODES

By Thornton C. Fry

Abstract

Potential distribution between parallel plane electrodes; Note regarding an earlier paper.—The objections raised by Langmuir (Phys. Rev. **21,** 419, 1923) to the results previously given (Fry, Phys. Rev. **17,** 441, 1921) were due to a misunderstanding of the meaning of the symbol $\overline{V}_0$, which is here explained in greater detail. Some typographical errors are also pointed out.

IN AN earlier paper[1] on this subject the writer presented a method of computing the relation between the space current and voltage when the initial velocities possessed by the electrons are not ignored. Dr. Irving Langmuir[2] experienced considerable difficulty in understanding certain parts of the paper, and as it is possible that others may have had the same difficulties it seems wise to attempt to clear the matter up.

The difficulty centers about the symbol $\overline{V}_0$ which was defined, except for the bracketed clause, as the "potential change $\overline{V}_0$ which would give to an electron an energy equal to the average energy [associated with the normal velocity components] of those shot out from the cathode." I had supposed that the bracketed clause was unnecessary because I had explained earlier in the paper that "the normal component and not the complete velocity will be dealt with." It appears, however, that the emphasis on this point was not sufficient to avoid misunderstanding.

My results were given in terms of this average energy, rather than the temperature, because the correct relationship between the temperature and the constants in Maxwell's equation was actually in question when my paper was written. The average energy, however, was connected with Maxwell's equation by a mathematical law. Hence, results expressed in terms of $\overline{V}_0$ were not likely to become obsolete. Now that the matter in question has been fairly well cleared up,[3] either method is feasible and, of course, both give the same results.

This same uncertainty made it unwise to "compute" the value of $\overline{V}_0$. Therefore, in choosing an illustrative example, the value 0.3,

[1] Fry, Phys. Rev. **17,** 441, April, 1921
[2] Langmuir, Phys. Rev. **21,** 419, April, 1923
[3] See Jones, Roy. Soc. Proc., A, **102,** p. 734; and Germer, Science, **57,** p. 392

which was known to correspond roughly to tungsten at 2400° K, was arbitrarily chosen. Langmuir calculates a value, 0.207, and uses this value in his example. The examples are therefore not stictly identical. The numerical differences, however, are not large enough to affect the conclusions to which the discussion led. Such as they are, they are attributable to this difference in assumed conditions, and not, as Langmuir supposed, to errors of calculation and confusion of averages.

It may be well to call attention to three errors which were not noticed in reading proof. The right hand side of the last equation on page 444 should be preceded by a negative sign. The exponent of π in the equation next preceding it should be 3 instead of 2. Also, the denominator of the right hand side of the second equation on page 449 should contain a π. These errors, being of a typographical nature, do not influence the subsequent work. The first two did not contribute to Langmuir's difficulty, but the third occurred in an equation relating $\overline{V}_0$ to the average initial velocity and undoubtedly added to the confusion caused by the other misunderstandings.

Since, when these matters are understood, Langmuir's objections vanish, it is unnecessary to take them up in detail. It need only be said that there is no exaggeration in the statement that the errors in the 3/2 power law "may be close to 50 per cent for voltages as high as 40 or 50 volts. At still lower voltages the 3/2 power law need not even give a rough approximation to the values to be expected from the Maxwell distribution." To be exact, in my illustration the difference was 42 per cent at 39 volts—the nearest tabular value—and larger errors were easily obtainable. In fact, without changing the plate voltage, the error could have been made as large as desired by increasing the electrode separation, though of course the example would soon have lost its practical importance.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND THE WESTERN ELECTRIC COMPANY, INC.,
August 15, 1923.

THE STRIKING POTENTIAL IN THE LOW-VOLTAGE MERCURY ARC

By M. Scott

Abstract

Striking potential in the low-voltage mercury arc.—(1) *Variation with vapor pressure.* A tube with a thoriated tungsten filament and a nickel anode over a reservoir of mercury was heated in an electric furnace. When a constriction was placed in the tube leading to the pump so as practically to eliminate streaming of the vapor, and the temperature raised, the striking potential decreased to a minimum of approximately 5.3 volts for a pressure corresponding to a mercury surface temperature of 160°C and then increased. When no constriction was present, a similar curve was obtained except that on account of the streaming the pressure for a given furnace temperature was lower and hence the minimum was not reached below 320°C. If the fact that the vapor was fresher in the second case had any influence, it was not evident. (2) *Variation with the distance away of mercury surface.* When streaming was prevented, the same striking potentials were obtained for the same vapor pressures whether the surface was 5 cm or 80 cm from the arc. These results are somewhat at variance with those of Yao and suggest that further investigation is necessary.

Part I

THE experiments here described were undertaken in order to obtain more definite knowledge regarding the characteristics of the low voltage arc and in particular regarding the factors upon which the striking potential depends. An effort was made to obtain as steady conditions as possible in the experimental tube with particular attention to securing gas-free apparatus, a good vacuum, and a conditioned filament that would yield a constant electron emission.

The plan of the original set-up used in these experiments is indicated in Fig. 1. The anode was a platinum wire (8 mil.) and the filament consisted of two parallel thoriated tungsten wires (10 mil.) about 15 mm long. The whole tube was completely enclosed in an electric furnace, whose temperature could be maintained constant within two or three degrees and was read by means of a mercury thermometer placed as indicated. The filament current was supplied by a set of storage batteries and was varied by means of a series resistance, the value being read on a shunted milli-voltmeter. The applied potential for striking the arc was obtained from a potentiometer arrangement and was measured by a Weston voltmeter. In all the work the potential was applied

first from the anode to the positive end of the filament and then from the anode to the negative end of the filament. In the curves, the average value of the potentials obtained with these two connections is plotted as the striking potential. The variation of the electron current or the arc current was observed by means of a galvanometer.

A second type of tube contained a cylindrical nickel anode in place of the platinum wire and had mounted upon the anode a thermo-junction by means of which the temperature of the anode could be obtained. A third type of tube, otherwise similar to the second, possessed a thermo-junction for measuring the temperature of the mercury near its surface.

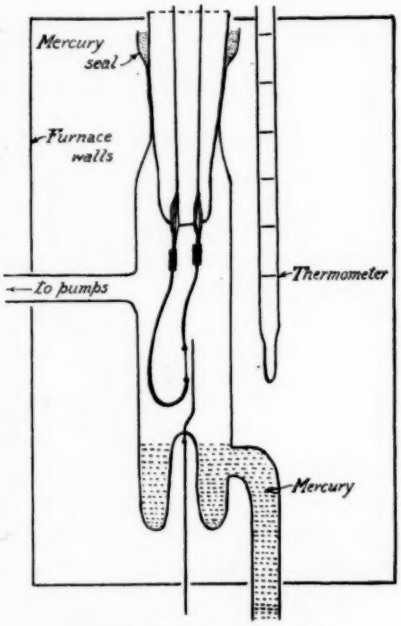

Fig. 1. Original apparatus

Before any measurements were made, the pumps, a mercury vapor pump combined with a Hyvac fore-pump, were kept operating while the apparatus was baked at 300° C, and the filament was glowed at a current higher than that to be used during the experiment. When the current in the anode-filament circuit remained constant for a period of two or three hours, the filament was considered ready for use. Another test was to strike the arc for an instant at intervals of several minutes and observe when the striking potential became constant. The arc must not be maintained for this will increase the striking potential measured during the succeeding few seconds.

The initial work consisted in a study of the variation in the striking potential with filament current, and before the report of the work by Compton and Yao,[1] results similar to theirs had been obtained by the writer, but were not reported because it was felt that the filaments then used, with their heavy currents, were not as yet sufficiently constant in their emission. This work covered not only the striking potential but also the breaking potential, and these results check well with Yao's published curves.[2] It has never been found possible to strike the arc at less than 5.5 volts, when initial velocities are considered, even though the arc may be maintained at well below 2 volts.

The difficulty in studying the variation in the striking potential with vapor density is to determine the value of the vapor density. Since condensation occurs in the side tube of the pump, there is a pressure gradient from the liquid surface to this tube. Also the filament is extremely hot and tends to decrease the vapor density in the region of the anode, which is probably the region of chief importance in striking the arc. It is, therefore, difficult if not impossible to get more than an idea of just what the vapor density is. Nevertheless it was felt worth while to obtain data, recording the temperature as given by the mercury thermometer and the corresponding striking potential.

The method of taking a set of data was to adjust the furnace current to give a desired value of the temperature and then to take readings of the temperature and the striking potential every five minutes until the temperature remained constant within 2 or 3 degrees and the striking potential within .1 volt. The operation was repeated at other temperatures. The temperatures chosen ranged from 70° C to 300° C, and readings were taken not only in steps of increasing temperature but also in steps of decreasing temperature. It was found that the striking potential was constant within .1 volt at a given temperature.

While many sets of data were taken, only one is completely plotted in Fig. 2, for that is typical of all the results obtained with the first and second types of tube. It is seen that above a certain temperature, 150° to 180° depending on the filament current, the striking potential decreases rather slowly but more or less uniformly with increasing temperature. If this decrease continues to higher temperatures, it would be possible to strike an arc at less than 5.5 volts. With regard to this point reference should be made to the work of Stead and Stoner on "Low-Voltage Glow in Mercury Vapor."[3] They found that the glowing potential, which

[1] Compton and Yao, Phys. Rev. **20**, 105, 1922
[2] Yao, Phys. Rev. **21**, 1, 1923
[3] Stead and Stoner, Proc. Camb. Phil. Soc. **21**, Feb. 1922

must certainly correspond to the striking potential of the arc, decreases more or less uniformly with increasing temperature from 15° C to 150° C and then rises. With the apparatus here described, it was impossible to go much above 300° C. It is not known whether the vapor pressure for 300° C was actually greater than that corresponding to 150° C, but it seems very probable that it was, in spite of the more rapid streaming of the vapor into the side tube at the higher temperatures.

The experimental tube used by Stead and Stoner was sealed from the pumps so that the mercury vapor was in equilibrium with the liquid, while in the writer's tubes, there was a streaming of vapor into the side tube, which became pronounced at temperatures above 150° C.

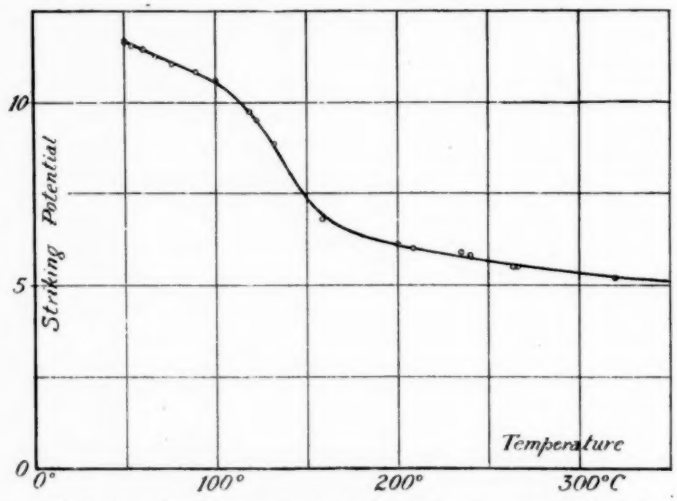

Fig. 2. Variation of striking potential with the temperature indicated by the mercury thermometer

It seems that the difference in the results obtained must be assigned to some factor that enters with the streaming of the vapor.

In order to reduce the uncertainty in the value of the vapor density, the third type of tube with the thermo-junction in the mercury was adopted. A difficulty developed at once, for due to the condensation in the side tube, there was a net evaporation from the liquid surface, which produced a large temperature gradient just below the mercury surface and extending downward for about one-half inch. Also the glass was hotter than the mercury and this set up convection currents in the mercury, and made the thermo-junction unsteady so that the temperature could not be accurately obtained. To eliminate these difficulties, it was planned to seal off the tube from the pumps at a point inside the furnace. With this in mind, a tube was inserted with a con-

striction for sealing off, and trial experiments were made with the pumps still connected. It was found that the constriction had eliminated condensation so far as our measurements were concerned, the thermo-junction became steady, and the mercury no longer possessed any temperature gradient at its surface.

Sets of data were taken in the manner previously described, and the results are shown in Fig. 3. The striking potential is plotted against the temperature as given by the mercury thermometer (curve A) and also as given by the thermo-junction (curve B). The difference in these temperatures is due to the high heat conductivity of the mercury column. The type of variation differs from that shown in Fig. 2 only at temperatures above 150° C and shows the same general character as the result obtained by Stead and Stoner.

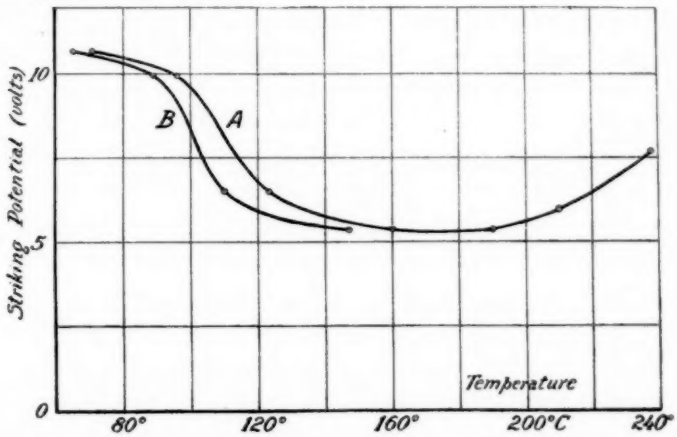

Fig. 3. Variation of striking potential with (*A*) mercury thermometer temperature, (*B*) thermo-junction temperature

It may be that the shape of the curve in Fig. 2, obtained with the first and second types of tube, can be explained on the basis that the increase in temperature and hence vapor pressure at the liquid surface produces a greater velocity of flow of vapor from the surface and results in younger vapor being present at the anode. Consequently on the basis of Yao's result that the striking potential is less with younger vapor, the striking potential would decrease with increase in temperature of the mercury surface, if this effect outbalanced the one evident in Fig. 3.

With the second type of tube it was found that if the arc were struck and maintained at a high voltage for a few seconds, the anode would become hot and the striking potential would increase as much as .3 volts; then, if the arc were struck at intervals of a few seconds, the striking potential would decrease with the temperature of the anode, until they

both reached their earlier values. This might be due either to a decrease in vapor density in the neighborhood of the anode or to a decreased electron emission of the filament after bombardment by the positive ions. Since Hebb observed a decrease in striking potential, when the platinum anode was heated, the effect is probably due to a decreased emission.

It is to be noticed in Fig. 2 that the striking potential—temperature curve consists of two more or less straight portions connected by a transition curve. While the data covering the whole range of temperatures were being taken, it was observed that the arc struck definitely and vigorously at temperatures below 85° C and also above 140° C. In the range between, the striking of the arc was attended by two or three potential drops as the applied potential was raised. At 100° C the first drop was most prominent but as the temperature was increased, the last one became relatively important until at 140° C it alone remained.

Since these facts were observed time after time it seems reasonable to assume that two types of arc are involved—the one existing at the lower temperatures and the second at the higher temperatures. It may be that at the lower vapor pressures the mercury entities find themselves in a condition sensitive to stimulation of the 6.7 volt type of radiation in preference to the 4.9 volt type, while at the higher vapor pressures the reverse is the case.

Part II

Y. T. Yao[2] recently described experiments to show that the striking potential of the low-voltage arc in mercury depends upon its distance from the liquid surface. It was found that the striking potential increased when the arc was struck in vapor at increasing distances from the surface. This result was expected on the basis of the work by Van der Lingen and Wood[4] on the fluorescence of mercury vapor.

These experimenters found that during distillation, the mercury vapor close to the liquid surface, when stimulated, radiates strongly light of wave-length λ2536 and that the intensity of the radiation depends upon the rapidity of the distillation and becomes faint when the vapor is in equilibrium with the liquid. It is to be expected, therefore, that this vapor during distillation will also favor the striking of the arc at a lower voltage. It is evident that the vapor is fresher on the average when distillation occurs than when the vapor is in equilibrium with the liquid. In some of his experiments, Yao seems to have taken precautions to prevent vapor streams and hence to obtain vapor in equilibrium with the liquid—a case which, on the basis of the above-described

[4] Van der Lingen and Wood, Astrophys. Jour. **54**, 149, 1921

experiments, might be expected to produce a condition favorable for striking the arc at a lower voltage only if the striking potential is a more sensitive test of the age of the vapor than the phenomenon of fluorescence.

In order to investigate farther under what conditions there is a variation in the striking potential with distance from the liquid surface the type of apparatus shown in Fig. 4 was adopted. It consisted of a cylindrical, nickel anode with a thoriated tungsten filament along the axis. A platinum-platinum rhodium thermo-junction was inserted at the upper and lower positions of the mercury level, in order that the temperature and hence vapor pressure of the mercury might be accurately known. In order that the two levels chosen might correspond to a large ratio of the distances from the liquid surface, a helix of 3/8 inch glass tubing was sealed in between these positions. These distances were 5 cm and 80 cm approximately. The whole was completely enclosed in an electric furnace and a mercury thermometer was inserted with its bulb opposite the anode so that the temperature could be read.

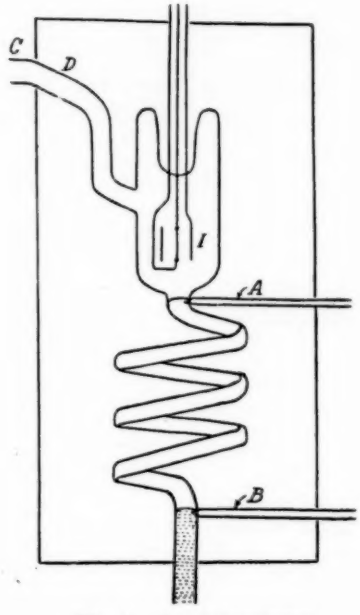

Fig. 4. Later apparatus

The treatment of the apparatus preparatory to an experiment was the same as described in Part I.

The experiment consisted in raising the mercury level to *B*, then while all conditions were maintained constant, in observing the striking potential at regular intervals until it was definitely determined within .1 volt. Next the mercury level was raised to position *A* and the process repeated. In general, the striking potential corresponding to position *A* was lower because the temperature of the mercury surface was higher, being higher in the furnace. Finally, the temperature of the furnace was lowered until the thermo-junction at *A* read the same as the one at *B* during the first step. The process of observing the striking potential at regular intervals was again repeated, other factors being kept constant, until the striking potential became constant within .1 volt. Sometimes the mercury level was first raised to position *A*, then lowered to position *B* and the furnace temperature increased so that the temperature

of the liquid surface was the same as it had been for position *A*. In Table I, the results for this order of procedure are indicated by a star.

In the apparatus, as indicated in Fig. 4, condensation was bound to occur in the side tube to the pump at *C*, but as there was a positive temperature gradient from the bottom to the top of the furnace, and as the mercury was always at a lower temperature than that of the furnace, no condensation could ever take place elsewhere than at *C*. This condensation introduced a pressure gradient for the mercury vapor and since the distance *IA* was much smaller than the distance *IB*, the vapor pressure at *I* was bound to be much greater when the mercury level was at *A* than when at *B*, provided the temperature of the mercury surface was the same in both cases. It was therefore expected that the striking potential would, for this set-up, be lower when the mercury level was at *A* than at *B*.

Table I summarizes data, which were taken with the apparatus as described. By change in furnace temperature is meant the change in temperature necessary to maintain the mercury surface at the same temperature for the level *A* as for the level *B*.

TABLE I
Results with streaming vapor

No.	Position	Temp.	Change in furnace temp.	Striking potential	Difference
1	B	110° C	15	8.92	2.2
	A	110° C		6.72	
2	B	119	9	6.97	1.2
	A	119		5.8	
*3	A	127	10	5.52	.8
	B	127		6.3	
*4	A	133	5.5	5.37	.5
	B	133		5.87	

It is seen that the difference in striking potential can be made as small as .5 volts for the ratio of distances employed, and in view of the difference in vapor pressure at the anode in the two cases, practically all of this difference might be assigned to that cause. These data then do not seem to allow of a more definite conclusion than that the striking potential difference might be accounted for by the difference in the vapor pressures and that the striking potential may or may not be a function of the distance from liquid surface to the anode.

The next step consisted in inserting a constriction in the side tube at point *D* (see Fig. 4) with the intention of sealing off the tube from the pumps. In order to make sure that no great gas pressure would develop so that the arc would behave erratically when the pumps were

disconnected, the striking potential was observed at five minute intervals for a period of two or three hours after the tube had been disconnected from the pumps by a mercury cut-off. The striking potential during this time did not change by more than .1 volt.

With this constriction in the side tube, it was found that at temperatures below 150° C the condensation in this tube was practically eliminated so that over a period of hours no visible drop of mercury collected here, while without the constriction a steady collection was easily observed. Under these circumstances, then, the pressure gradient was practically reduced to zero, even without sealing off from the pumps, and with this in mind, the experiment was repeated as previously described. Observations were made at three different temperatures. The results are tabulated in Table II.

TABLE II

Results with constriction in connection to pumps

No.	Position	Temperature	Striking potential
1	B	70.5	10.15
	A	101.0	7.97
	A	70.5	10.15
2	B	105	7.0
	A	105	7.0
3	B	146	5.07
	A	146	5.07

It is seen that when the temperatures of the mercury surface were the same for the two positions so that the vapor pressures were the same, the striking potentials were identical within .1 volt. The conclusion to be drawn is two-fold: first, that the striking potential is not appreciably more sensitive than the phenomenon of fluorescence for detecting the younger vapor; second, that in mercury vapor which is in equilibrium with its liquid, the striking potential is not a function of the distance to the liquid surface, at least for the distances used.

It would seem that further experimentation is necessary to prove that the striking potential depends upon the age of the vapor and that the striking of the arc may be used to indicate that the young vapor in a stream is especially sensitive to $\lambda 2536$ stimulation.

Acknowledgment is made to the General Electric Company for the thoriated tungsten wire furnished by them. Also I wish to express my thanks to Professor R. C. Gibbs for his interest and many suggestions.

CORNELL UNIVERSITY,
May, 1923.

THE PHOTO-ELECTRIC EFFECT OF CAESIUM VAPOR

By Jakob Kunz and E. H. Williams

Abstract

Long wave-length limit for photo-electric emission from caesium vapor.— Using a special quartz tube and taking precautions to avoid photo-electric emission from the electrodes, a narrow beam of nearly monochromatic light of gradually decreasing wave-length, was focused on the hot caesium vapor, and it was found that above 3220 A the emission was zero, between 3220 and 3145 A the emission changed linearly because of the width of the slit used, and below 3145 A the emission was practically constant. The mean, 3180 A, is taken as the critical wave-length. This is evidently identical with the convergence wave-length 3184.28 A, which is related to the ionization potential V_i according to the equation $V_i = hc/e\lambda_i$. Therefore the separation of an electron from a caesium atom requires the same amount of work whether produced by an impinging electron or by absorption of light.

THE convergence frequency ν_i of the principal series $(1s)-(mp)$ of caesium vapor is given by

$$\nu_i = c/\lambda_i = 3\ (10)^{10}/3.1843\ (10)^{-5}.$$

It has been shown by Foote and Mohler that the ionization potential V_i of caesium vapor is 3.9 volts while the equation $V_i e = h\nu_i$ gives 3.877 volts. If the separation of an electron from an atom of caesium vapor requires the same amount of work, whether carried out by an impinging electron or by absorption of light, then we should expect that light of wave-length 3184.28 A would be necessary to produce the photo-electric effect of the vapor, while light of longer wave-length would give no effect. This conclusion was tested and found to be true by experiments made with caesium vapor by the authors several years ago.[1] During the last winter we have been enabled by the use of a quartz tube with plane parallel end plates supplied to us by the research laboratory of the General Electric Company to repeat the experiments with greater precision.

The experimental determination of the photo-electric effect of metallic vapors and gases involves considerable difficulties. The most serious one consists in the fact that a trace of scattered light within the tube produces photo-electric emission from the metallic electrodes and glass walls covered with alkali metals which is 100 and 1000 times larger than the effect in the vapor itself. Even scattering of the light by the atoms of the vapor is to be feared, but it was found to be absent in the

[1] Williams and Kunz, Phys. Rev. **15**, 550, 1920

experiments to be described. Only small retarding and accelerating potentials can be used; otherwise the moving electrons would acquire sufficient energy to produce ionization by collision. It was thought advisable to measure the positive ions of the caesium vapor, and it was necessary to distinguish between the loss of electrons and the acquisition of positive charges by the plate connected to the electrometer. Surface effects have to be avoided by guard rings, and the thermionic emission from the deposited alkali metal on the electrodes and glass walls must be balanced or separated from a purely photo-electric effect. The temperature of the tube has to be as high as possible, in order that the vapor pressure may be as large as possible, but at high temperatures the caesium vapor begins to attack the quartz, rendering the inner surfaces conductive.

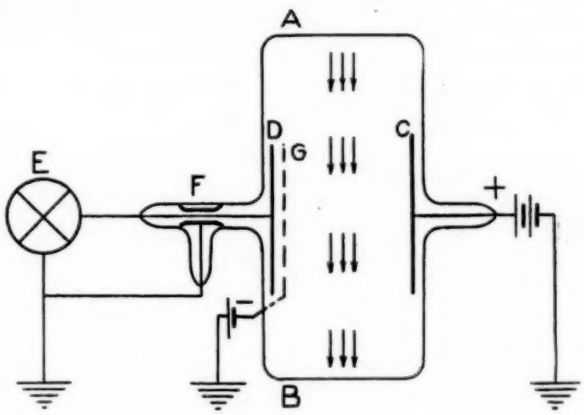

Fig. 1

The Physical Review **21**, 107, 1923, contains an investigation by R. C. Williamson on the ionization of potassium vapor by light. His results are in agreement with our previous observations and with our present experiments. His interesting method suggests the possibility of heating the metallic vapor in a vessel to a considerable temperature, then letting the vapor expand adiabatically and subjecting it to light of frequency ν_k. Condensation might occur as in the corresponding experiment by Wilson.

Apparatus

The essential part of the apparatus used in testing the photo-electric effect of caesium vapor was a quartz tube AB, with the necessary electrodes, shown diagrammatically in Fig. 1. The tube, which was 13 cm long and 6 cm in diameter, had plane quartz ends which produced practically no distortion of the light passing through. A guard ring F

surrounded the electrode D which was connected to the electrometer. The purpose of the grid C was to eliminate the possibility of photo-electric emission from the metal electrode D due to any scattered light that might strike it. The grid G was kept at a negative potential so that no electrons could leave D even though they were produced. The electrodes were of platinum, whose photo-electric threshold is 2800 A, sufficiently removed from the critical wave-length 3184 A.

Light from a Cooper-Hewitt quartz arc was passed through a Hilger quartz prism spectroscope and used as the ionizing agent. The width of the window in front of the tube was such as to permit light of a range of about 80 A to pass through the tube. A quartz converging lens between the window and the tube condensed the rays into a narrow beam.

The arrangement of the detecting part of the apparatus is also shown in Fig. 1. The connections are such that the electron of any ionized atom will go to the plate C and the positive ion to the plate D after passing through the negative grid G, which was of about 5 mm mesh. A few ions, of course, would be lost to the grid. If any light were to fall on the electrode D, negative electrons would be thrown out, and this, it is evident, would produce the same effect on the electrometer as though the plate D were to receive positive ions. Stray light was avoided as much as possible because the photo-electric effect of metals is large compared with that of vapors.

Results

A number of series of readings were taken in most of which the results were positive, i. e., light below a critical wave-length produced a photo-electric effect whereas light above the critical wave-length produced no effect. The procedure was to throw the light on for a given period (from one to five minutes) and then shut it off for the same period, observing in the meantime the drift of the electrometer. Observations were made at temperatures ranging from 140° C to 200° C. In starting any series of readings the first tests were made at 3360 A and 2530 A. It was soon found that the critical region lay between 3250 A and 3130 A. In practically all of the observations it was noted that the effect for the first interval of time, say one half minute, was greater than for subsequent intervals of time.

The first observations were made with light of wave-length well above and well below the critical wave-length. The effect was zero in the former case, quite strong in the latter case.

Tables I and II give the results of two series of readings. The effect at each point is the mean of several readings. In order to obtain the

wave-length where ionization takes place, a curve was drawn between the wave-length and the deflection of the electrometer. The results in Table II, which proved to be the most regular, were chosen for this purpose and the resulting curve is shown in Fig. 2. Since the effect

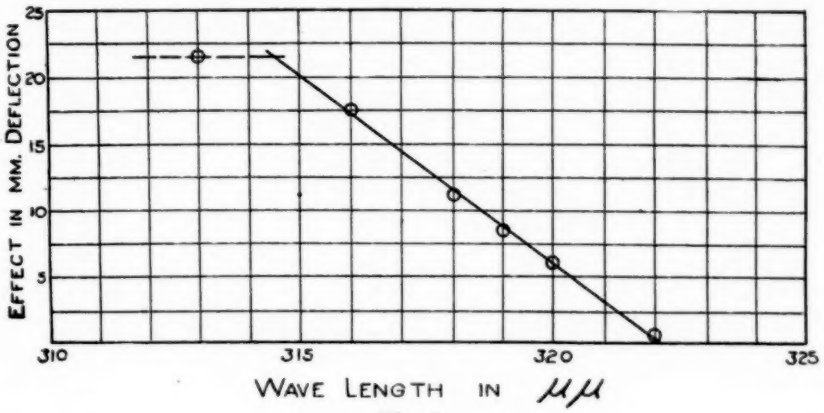

Fig. 2

begins when the edge of the window opening is at the critical wave-length and is a maximum when the entire window has reached that

TABLE I

λ	T	Deflections (5 min. periods)
3130A	140°C	21.3 mm.
3180	140	10.5
3190	140	8.3
3200	140	3.0
3220	140	.9
3250	140	.0
3360	140	.0

TABLE II

λ	T	Deflection (2 min. periods)
3360A	154°C	.0 mm
3250	155	.0
3220	158	.6
3200	160	6.0
3190	160	8.4
3180	160	11.1
3160	161	17.5
3130	161	21.5

point, the position of the critical wave-length as read by the middle of the window opening will be half way between where the effect begins and where it is a maximum. Applying this to Fig. 2 we obtain 3183 A for the critical wave-length or that wave-length above which no ionization takes place and below which ionization does take place. This is remarkably close to the theoretical value, even closer than the experimental sources of error would lead one to expect.

Other curves very similar to that shown in Fig. 2 gave the same critical wave-length of 3180 A. The part of the curve to the left of 3140 A need not necessarily be straight nor parallel to the X-axis but the results of other observations indicate that the effect at 2530 A is not widely different from that at 3130 A.

Our measurements therefore show that λ_i is between 3160 and 3200 A and is probably close to 3180 A. Within the limits of experimental error, this agrees with the convergence frequency 3184.28 A.

If light of the convergence frequency ν_i is able to raise the electron from the level *1s* to the level ∞ *p* or clear out of the atom with zero velocity, then the question arises whether light of higher frequency will also produce a photo-electric effect. In this case the electron would leave the atom with an initial velocity given by:

$$\tfrac{1}{2}\, mv^2 = h\nu - h\nu_i$$

Evidently this effect is very different from what we should expect from any classical resonance theory. But that this effect exists is probable from the discovery by R. W. Wood of the absorption band which extends from the convergence frequency toward higher frequencies. But even if it is found that the photo-electric effect exists for frequencies higher than ν_i, the question still remains whether the whole absorption of light is due to the photo-electric effect or whether the photo-electric effect is only an accompanying effect of absorption. In the former case we would have from the conservation of energy

$$E_a = neV_i = IV_i$$

Where E_a is the energy of light of wave-length, λ_i absorbed per unit time, n the number of electrons liberated per unit time, and I the electronic current. We are engaged in the further test of this equation, which should be independent of the temperature of the vapor. On the other hand, if only a part of the absorbed energy were transformed into electric energy by the separation of an electron from the atom, how could an atom of the Bohr type take up the rest of the energy of frequency ν_i in such a way as to raise the temperature of the gas?

The question of absorption of light is also important in connection with the resonance potential V_r which is given by $V_r e = h\nu_r$ where $\nu_r = c/\lambda_r = (1s) - (2p)$ is the first line of the principal series. Theoretically two resonance potentials are possible corresponding to the two levels p_1 and p_2, but so far only one resonance potential has been measured. Moreover we should expect, on the basis of the theory of the Bohr atom, that by means of electronic bombardment of increasing velocity or with light of decreasing wave-length we should be able to detect resonance potentials according to the energy levels *3p*, *4p*, *5p*. . . . With each higher resonance potential one to two more lines should be emitted and when finally ionization sets in, all lines of the principal series should be given out. Experiments in this direction are still in progress.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
April 20, 1923.

SPECTRO-PHOTOELECTRICAL EFFECTS IN ARGENTITE THE PRODUCTION OF AN ELECTROMOTIVE FORCE BY ILLUMINATION

By Paul H. Geiger

Abstract

Electromotive force produced by illumination of argentite.—If argentite (Ag_2S) is connected in a closed circuit with a galvanometer and one surface of contact is illuminated, an e.m.f. is produced which increases with the intensity, reaching a limit of about .013 volt for 600 candle-meters and over. On continued exposure, marked fatigue is shown, the e.m.f. decreasing in a few minutes to half value. By use of a monochromatic illuminator and a suitable intensity control, the e.m.f. was found to show a sharp maximum for about 1μ. The results were found independent of the contacts used whether Cu, Al, Fe, Sn, Ag or water. The effect is clearly not thermoelectric. Various samples showed similar results. No transmitted light effect was observed. *Six other minerals* showed the effect to a greater or less extent, including molybdenite (MoS_2) and acanthite (Ag_2S).

Resistance of argentite.—(1) *Variation with voltage.* The resistance, measured instantaneously was only half as great for 20 as for 4 volts. The resistance is about 4/5 as great in the light as in the dark, the ratio being independent of voltage. (2) *Variation with time of current flow.* The resistance increased with time, the crystal finally reaching a state when it was no longer light sensitive. Recovery was slow.

Introduction

BROWN, Sieg, Pfund, Coblentz and many others have studied the change of resistance of various substances, notably selenium, with change of illumination. T. W. Case[1] has discovered some twenty different crystalline substances which show an increase in conductivity with illumination. Kennard and Dieterich[2] found that the contact potential (measured on open circuit) varied with the intensity of illumination.

This investigation was undertaken with the purpose of studying the electrical and photoelectrical properties of argentite, a natural mineral whose chemical composition is given by the formula Ag_2S. After the work was well under way, a new and unexpected property was discovered.[3] This was the production of an electromotive force in a closed circuit consisting only of a galvanometer and a piece of argentite, when light fell upon one of the contacts on the crystal. This phenomenon was studied in detail; the effects were recorded for different

[1] T. W. Case, Phys. Rev. **9**, 305, 1917
[2] E. H. Kennard and E. O. Dieterich, Phys. Rev. **9**, 58, 1917
[3] H. H. Sheldon and P. H. Geiger, Phys. Rev. **19**, 389, 1922

intensities, for different wave-lengths, and for different metals and water as contact materials.

Some twenty different pieces of argentite were secured. These were not isolated crystals but were crystal conglomerates, so no effort was made to study the various properties along different crystal axes. The specimens varied in length from 5 to 20 mm, and in width from 3 to 8 mm. Samples were secured from the following localities: Batopilas, Mexico; Arispe, Sonora, Mexico; Freiberg, Saxony, Germany; and Schneeberg, Saxony, Germany. The crystals were kept in a desiccator in order that moisture would not affect the results. All of the results given in this paper have been checked with crystals differing greatly in appearance and coming from different regions, so it is assured that the results recorded hold true for argentite in general, not merely for individual specimens.

Production of an E.M.F. in a Closed Circuit by Illumination

To study the circumstances of the appearance of a current when a crystal was illuminated, a d'Arsonval galvanometer (Leeds and Northrup, high sensitivity) was connected directly to two knife edge contacts on the crystal. It was found that illuminating one contact gave a deflection in one direction and illuminating the other contact gave a deflection in the opposite direction. Illuminating the center of the crystal gave no deflection if the two contacts were shaded or equally illuminated. A number of tests were made which showed conclusively that the e. m. f. produced was not a thermoelectric force.

Tests on other minerals. All the available pieces of argentite were tested and found to produce an electromotive force upon illumination. Specimens of the following kinds of minerals also gave a deflection on illumination, although, in almost every case, smaller than that obtained with argentite: proustite (Ag_3AsS_3) ; pyrargyrite (Ag_3SbS_3); bournonite [$3(Cu_2,PbS)\ Sb_2S_3$]; molybdenite (MoS_2); stephanite (Ag_5SbS_4); acanthite (Ag_2S).

Specimens of the following, although listed by Case[1] as among those showing a change of resistance with light, failed to give a deflection large enough to be detected: galenite (PbS); stibnite (Sb_2S_3); polybasite (Ag_4SbS_6). One sample of cuprite (Cu_2O) showed the effect to a remarkable extent, while two others failed to give a perceptible deflection.

Crystal Fatigue as a Result of Constant Illumination

The deflection of a galvanometer connected to two contacts on an illuminated argentite crystal does not remain constant during the time

the light is on, but gradually decreases. When the light is turned off the galvanometer will usually swing back past the original zero nearly as far as the deflection made when the light was first turned on. Under some conditions, when the crystal was illuminated for a short time, the galvanometer would start to swing in one direction, then would reverse, the first swing reaching a value about one fourth of the total final swing. On turning the light off, the procedure was reversed, i. e., the galvanometer gave an increased reading before going back to zero.

Fig. 1 shows graphically the behavior when the light is supplied for a long period of time. Here the deflection, after a maximum at the start, gradually decreased to a point below zero. After about 8 minutes the light was turned off, resulting in a deflection in the same sense as

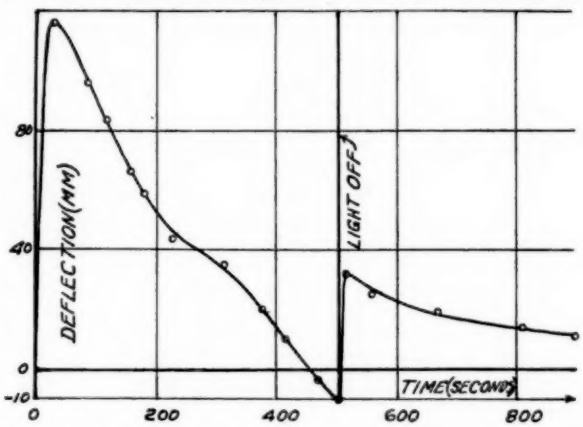

Fig. 1. Galvanometer deflection with continued exposure

when the light was turned on. Since the galvanometer was critically damped and since its ballistic period was 13 seconds, the actual rise of the current immediately after the illumination ceased was probably greater and faster than is indicated by the curve. A short time after this 8 minute exposure, the crystal was found to be greatly fatigued; only a quarter of the usual effect could be secured by turning on the light. A study of Fig. 1 makes it evident that there can be no continuous transformation of light energy into electrical energy by this means.

Variation in Electromotive Force with Varying Intensities of Illumination

Fig. 2 shows how the e.m.f. produced by light varies with the light intensity. One contact on the crystal was carefully shielded from the light, the other was illuminated by a 16 candle power automobile headlight. The intensity was varied by changing the distance between

the lamp and the crystal. The filament area was so small that it could be considered a point source, so the relative intensities of illumination on the crystal could be calculated from the inverse square law. An ammeter was used to keep the filament current constant. Especially for high intensities, the resistance of the crystal would not remain constant and variable thermoelectric forces would be introduced which would affect the results so that the galvanometer deflections would not be proportional to the electromotive forces produced by light. For this reason, measurements of the e.m.f. generated were made by a potentiometer method; a measured current flowing through a known resistance placed in the galvanometer circuit, being adjusted until the galvanometer gave zero deflection. By balancing out the thermoelectric

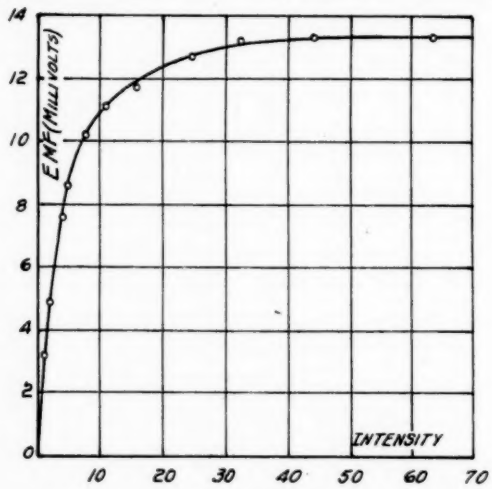

Fig. 2. E.m.f. as function of intensity

forces while the crystal was unilluminated and subtracting algebraically the value thus obtained from the value found with the crystal illuminated, the actual e.m.f. was determined. The unit of intensity used in Fig. 2 is arbitrary, being the intensity produced by the lamp at a distance of one meter. It is seen that only for the smaller intensities does the proportionality between the e.m.f. and the intensity hold true. This curve also shows that a limiting e.m.f. of 0.013 volt was produced.

Wave-Length Sensibility Curves

In order to find the comparative effect of radiations of different wave-lengths upon the production of the electromotive force, apparatus to give light of different wave-lengths, each with the same energy content, was constructed. Fig. 3 represents diagrammatically the equipment used. The light source was a 110 volt 400 watt stereopticon lamp with

a plane filament. The lamp was so oriented that the image on the slit B made by the convex lens A was nearly linear. The filament current was furnished by a 130 volt storage battery; this voltage being used because more than normal brilliancy was required at times. A 60 degree, 8 cm carbon disulphide prism with glass sides was used to obtain the desired dispersion. The monochromatic light selected by slit D fell on the concave spherical silvered mirror M which could be rotated so that the monochromatic light would be focused on either the crystal or a thermopile. The crystal was connected as before to the high resistance galvanometer. A low resistance d'Arsonval galvanometer was connected to the thermopile as shown. In order to obtain sufficient energy to give suitable deflections, the slits were made over a millimeter in width.

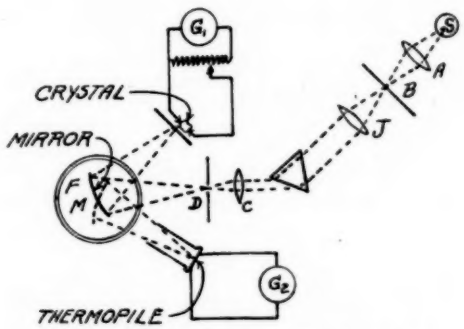

Fig. 3. Monochromatic illuminator

The calibration was accomplished by calculation, using the values for the index of refraction of carbon disulphide found in the Tables of Landolt, Börnstein und Meyerhoff. This calibration was checked experimentally by using fused salts which gave strong isolated spectral lines.

In order that equal light energies should fall on the crystal for each setting of the spectrometer, the current flowing through the lamp was regulated to the value which would give, for each spectrometer setting, equal amounts of energy as measured by the thermopile. The lamp was recalibrated several times as the work proceeded in order to avoid changes due to the aging of the filament. It was found however that no appreciable change occurred.

To obtain the first spectral sensibility curves a crystal was clamped between two copper clamps with knife edges. The values of the galvanometer deflections with differing wave-lengths are shown in Fig. 4. Similar curves were taken using samples of argentite from different regions of

the world. In every case the results showed a maximum effect to be produced by radiation of wave-length 1μ.

It was thought that perhaps the metal used as a contact material had an influence on the spectral selective effect, so contact jaws of aluminum, iron, tin and silver were made and used. It was found that in every case, the maximum of the sensibility curve was at the same place.

Water was also used as a contact material. For this part of the investigation a crystal was partially immersed in distilled water contained in a glass rectangular cross section. The water acted as one of the contacts, a copper plate immersed in it being connected to the galvanometer. The other contact was made by winding a fine wire tightly

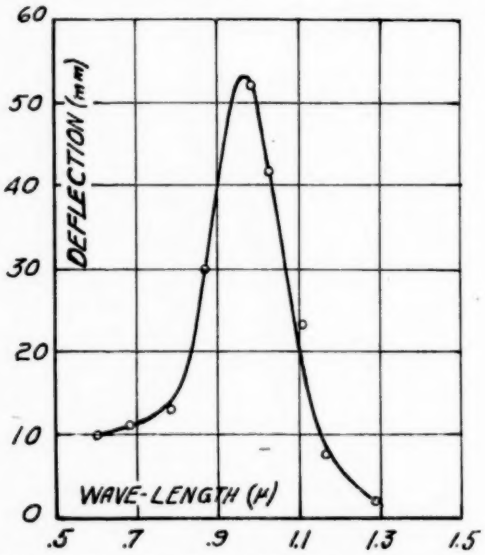

Fig. 4. Wave-length sensibility curve of argentite

about the crystal. The light passed through one side of the glass dish and through about 3 mm of water before reaching the crystal. Since radiations of different wave-lengths are reflected and absorbed by glass and water to different extents, the values of the filament current for each spectrometer setting had to be redetermined. A water cell 3 mm thick was placed in front of the thermopile and the filament currents which gave equal light energies as then measured by the thermopile were recorded. Since it was necessary that the path of the light reaching the crystal be equivalent to the path traversed in going to the thermopile, the dish in which the crystal was to be immersed was made with the front face composed of two pieces of glass each of the same thickness as the sides of the compensating cell.

Each time the galvanometer was first connected to an immersed unilluminated crystal, a very large deflection resulted. Wave-length sensibility curves taken under this condition showed a maximum effect in the visible spectrum. The crystal was extremely sensitive to light at these times. After the crystal had been connected in a closed circuit for eight or ten days the counter e.m.f. decreased to a small value and the maximum effect was found to be at 1μ as before. When water was used as a contact material much larger deflections were obtained than when any of the metals were used. This was probably due to the better contact and the larger area illuminated.

The sensitivity of argentite to radiations in the near infra-red suggests that a cell for use in some infra-red research might be constructed which would offer several advantages.[4]

Increase of Resistance with the Time of Flow of Current

When the properties of argentite were first being studied, it was found that when a crystal was placed in one arm of a Wheatstone bridge a balance could not be secured. If the galvanometer circuit was kept closed the galvanometer made erratic movements. The usual steps were taken to render the galvanometer steady; such as shielding, carefully insulating the wiring, thoroughly drying the crystal, etc. It was thought that perhaps the heating effect of the bridge current caused the irregular deflections, so the battery was connected continuously for several days. Measurements made then showed that the resistance had become extremely great. After a number of tests it was found that the resistance of any piece of argentite would increase with the time of flow of current through it.

Measurements of the resistance of the crystal at different known times after the bridge current was turned on, were made almost instantaneously by inserting the galvanometer in the bridge circuit for a definite short period by means of a Helmholtz pendulum. By substituting a known variable resistance for the crystal and adjusting it until the same deflection was obtained as when the crystal was in circuit, all other factors remaining the same, the desired resistance determination was made.

This study showed that the resistance increased with the time of flow of current; that the time taken for a crystal to reach the final condition

[4] Since the above results were obtained, there has appeared in the Bulletin of the Bureau of Standards, (Scientific Paper No. 446) an article by W. W. Coblentz entitled, "Spectrophotoelectrical Sensitivity of Argentite, (Ag_2S)." In this article the change of resistance with illumination is discussed at length. It was found that the maximum change in resistance per unit radiant energy was due to radiation of wave-length 1.35μ at ordinary temperatures, and 1.1μ at very low temperatures.

depended on its previous electrical history; that the time for recovery was long; that the increase in resistance was confined to portions carrying the greater share of the current; that the crystal was not light sensitive after a current had flowed through it for some time.

Variation of Resistance with Potential

Brown,[5] Pfund[6] and others have shown that some light-sensitive substances exhibit a change in resistance with a change in applied potential, and therefore tests for this effect were made on argentite. The work was complicated somewhat because the current necessary to make the observations would increase the resistance if allowed to flow for an appreciable time. The usual Wheatstone bridge arrangement was used with the exception that the galvanometer was connected permanently in the circuit and the battery current turned on for a definite short interval by means of the Helmholtz pendulum. The circuit was found to be non-inductive by a preliminary test, so no error was introduced by connecting the galvanometer before the battery was connected. A rheostat in the battery circuit was adjusted to give the desired voltage over the crystal, the pendulum was released and the resulting galvanometer deflection recorded. The value of the resistance was determined by substitution as before. The process was repeated, working from 1 volt upwards to 20 volts.

Since current was flowing through the crystal for only about 1/10 second for each determination and since the potential was raised for each succeeding measurement, it seemed unlikely that the results would be vitiated to any appreciable extent by the flow of current through the crystal; but to make certain, the curve was repeated, this time allowing at least 24 hours between each reading. The curve thus obtained was identical with the first. If any error of this sort did appear, it would mean that a higher value for the resistance would be obtained for the greater voltages, so it is sure that there is a decrease in the resistance with an increase in potential difference.

The upper curve in Fig. 5 shows how the resistance changes with potential difference when the crystal is protected from light. The lower curve is the same except that the crystal was illuminated by a 25 watt tungsten lamp through a 2 cm water cell. In obtaining the data for this curve the contact jaws were shielded from the light, so that the resistance measurements would not be affected by the e.m.f. produced by light. The current was turned on the lamp by a contact on the

[5] F. C. Brown, Phys. Rev. **4**, 85, 1914
[6] A. H. Pfund, Phys. Rev. **7**, 295, 1916

Helmholtz pendulum. From the data from which these two curves were plotted, the change in resistance (due to light) per unit resistance was calculated for different values of the potential difference. It was found that this ratio was a constant, within experimental error, over the range of voltages covered, i. e., from 1 to 20 volts.

The Transmission of the Light Effect

In 1913 Brown and Sieg,[7] working with isolated crystals of selenium, found that when light fell upon a portion of a crystal, the resistance of a remote portion of that crystal was reduced. No evidence of such a transmitted light action was found in argentite, although it was looked

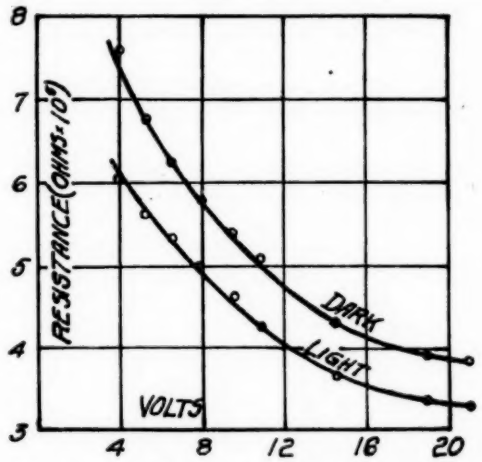

Fig. 5. Variation of resistance with potential

for and could have been detected by the methods used even if it had existed only to a much smaller extent than had been found for selenium. Perhaps if a sufficiently large isolated crystal could be secured the effect would be found. Pfund[8] found that there was no transmission of the light effect in cuprous oxide; and Coblentz[9] found none in molybdenite.

In conclusion, the writer wishes to express his thanks to Dr. H. H. Sheldon who suggested the interesting possibilities in the study of crystal conduction and who gave aid during the time the work was being done.

University of Michigan Physical Laboratory,
Ann Arbor, Michigan,
January 27, 1923.

[7] F. C. Brown and L. P. Sieg, Phil. Mag. **28**, 497, 1914; Phys. Rev. **4**, 85, 1914
[8] A. H. Pfund, Phys. Rev. **7**, 298, 1916
[9] W. W. Coblentz, Bull. Bur. of Stds. **15**, 121, 1919

ROTATIONAL SPECIFIC HEAT AND HALF QUANTUM NUMBERS

By Richard C. Tolman

Abstract

Application of half quantum numbers to the theory of the rotational specific heat of hydrogen.—It is shown from a consideration of infra-red rotation-oscillation spectra, that the lowest possible azimuthal quantum number for a non-oscillating rotating molecule of the rigid "dumb-bell" model can have only the values zero, one, or one-half. An elementary theory of quantization in space for the new case of half quantum numbers is then developed which shows that the a priori probabilities for successive levels of rotational energy stand in the ratios of 1, 2, 3, ... The specific heat curve for diatomic hydrogen to 300°K is then calculated on the basis of the energy levels and of a priori probabilities corresponding to half quantum numbers, and is compared with the experimental points and with the curves calculated by Reiche using zero and one as the lowest possible azimuthal quantum number. At low temperatures the new curve agrees with the experimental data as well as any curve of Reiche's. At the higher temperatures, none of the curves agree with all the experimental points. *The moment of inertia for the hydrogen molecule* corresponding to the new curve is $J=1.387\times10^{-41}$ gm cm², about two-thirds the values assumed by Reiche, 2.095 to 2.293×10^{-41}, and agrees better with the conclusion of Sommerfeld from the separation of lines in the many lined spectrum of hydrogen, that the moment of inertia of an excited hydrogen molecule is 1.9×10^{-41} gm cm², which should be greater than that of the unexcited molecules involved in specific heats. Hence the possibility of half quantum numbers seems worthy of consideration.

Introduction

IT IS the purpose of the following paper to investigate the possibility of accounting for the rotational specific heat of diatomic hydrogen by assuming for the hydrogen molecule the rigid "dumb-bell" model with two degrees of freedom, making use of the "first" form of the quantum theory, and taking the lowest possible azimuthal quantum number as one half instead of either zero or one as has previously been done.

We shall first show from a consideration of infra-red rotation-oscillation spectra, that the only possible values for the lowest azimuthal quantum number for the non-oscillating molecule are zero, one half, and one, and shall point out that the new assumption has the advantage of making the lowest azimuthal quantum number one half for both the oscillating and non-oscillating molecule, instead of different for the molecule in the two states. We shall then develop an elementary theory

of quantization in space for half quantum numbers and show that such a theory leads in a very simple and unconstrained manner to a priori probabilities for successive energy levels which stand in the ratios 1, 2, 3, 4 etc. Using the new a priori probabilities and new energy levels, the specific heat curve for hydrogen will then be calculated and compared with the experimental data of Eucken[1] and of Scheel and Heuse.[2] The results will also be compared with those calculated by Reiche[3] on the assumptions of zero and one as the lowest possible azimuthal quantum number, and various assumptions as to a priori probabilities.

The new specific heat curve thus obtained agrees with the experimental points at low temperatures as well as any curve of Reiche's, and has the advantage of giving a lower value for the moment of inertia of the hydrogen molecule, a result which is supported by the separation of the lines in the many-lined spectrum of hydrogen. At higher temperatures neither the new curve nor those of Reiche agree completely with the experimental points.

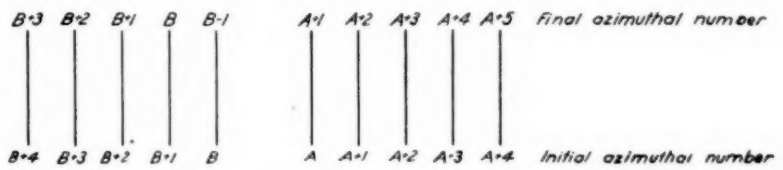

Fig. 1

It has seemed worth while to present the results of the calculations since half quantum numbers have recently shown a surprising tendency to appear, and have already been considered by Kratzer[4] as a definite possibility in attempting to account for band spectra. It is believed that the results are sufficient to show that half quantum numbers must also be regarded as a definite possibility in attempting a theory of rotational specific heats.

Rotational Quantum Numbers and Infra-Red Spectra

Information as to the possible states of rotation of a diatomic molecule can best be obtained from a consideration of the rotation-oscillation spectra of the hydrogen-halides. These spectra consist of approximately equally spaced lines with the omission of one line in the center as shown diagrammatically in Fig. 1.

[1] Eucken, Sitzungsber d. Preuss. Akad. d. Wiss. 1912, p. 148
[2] Scheel and Heuse, Ibid. 1913, p. 44; Ann. der Phys. **40**, 473 (1913)
[3] Reiche, Ann. der Phys. **58**, 657 (1919)
[4] Kratzer, Ergebnisse der Exakten Naturwissenschaften **1**, 332, 1922

Except for a possible uncertainty as to the correct way of assigning rotational quantum numbers to the different lines, the theory of such spectra has been presented by Kratzer[5] in a very satisfactory form, which not only takes account of the rotation of the molecules about their center of gravity and the oscillation of the atoms along their connecting line but also allows for the mutual interaction of rotation and oscillation and for the possibility that the law of force between the atoms may be such as to lead to non-harmonic oscillation.

For our immediate purpose we shall not need the complete theory but may consider that the energy taken up by the molecule accompanying an *absorption* line in the fundamental series is given by the approximate equation

$$h\nu = h\nu_0 + (m'^2 - m^2)h^2/8\pi^2 J \qquad (1)$$

where ν is the frequency of the line, ν_0 the frequency of the oscillation, m and m' the azimuthal quantum numbers before and after absorption, and J the moment of inertia of the molecule. Using the Bohr selection principle to restrict the change in azimuthal quantum number to the values

$$m' = m \pm 1 \qquad (2)$$

it can easily be shown that Eq. (1) does lead to a set of equally spaced lines, the *absorption* lines of higher frequency (to the right of the gap), being associated with unit increase in azimuthal quantum number and the lines to the left of the gap being associated with unit decrease in azimuthal quantum number, and furthermore the initial azimuthal quantum number of the molecule before absorption increasing by unity for each successive line counted from the center outwards.

We may use the above results to assist us in determining the possible absolute values for the initial quantum numbers. Referring again to Fig. 1, let the initial quantum numbers for the lines to the right of the gap be A, $A+1$, $A+2$, . . . and for those to the left of the gap to be B, $B+1$, $B+2$, ... where A and B are the two unknown quantities concerning which information is desired.

Since the interval between the lines with initial quantum numbers B and A is twice that between the lines A and $A+1$, it is evident from Eq. (1) that we may write the equation

$$[(A+1)^2 - A^2] - [(B-1)^2 - B^2] = 2[(A+2)^2 - (A+1)^2] - 2[(A+1)^2 - A^2]$$

which reduces to

$$B + A = 2 \qquad (3)$$

Furthermore, since we accept the hypothesis that quantum numbers

[5] Kratzer, Zeitschr. f. Phys. **3**, 289 (1920)

can only differ by an integer, we may write for the difference between B and A, the equation

$$B-A=i, \text{ where } i=0, \pm 1, \pm 2, \text{ etc} \qquad (4)$$

Let us now examine the different possible cases that can be obtained by taking different values for i.

Case I. $i=0$; $A=B=1$.

This is the assumption originally made by Kratzer.[5] It makes the lowest possible quantum number unity for a non-oscillating molecule and, since $B-1$ occurs after absorption, zero for an oscillating molecule, and thus has the disadvantage of allowing zero rotation in one case but not in the other.

Case II. $i=1$; $A=\frac{1}{2}$; $B=3/2$.

This is the case we shall test in this paper. It makes the lowest possible azimuthal quantum number one half, the same for oscillating and non-oscillating molecules.

Case III. $i=2$; $A=0$; $B=2$.

This case would allow zero rotation for the non-oscillating molecule but not for the oscillating molecule, which is inherently improbable and has been shown by Reiche to lead to impossible specific heat curves.

It can easily be seen that cases where i is assumed negative or numerically greater than two are not feasible.

Quantization in Space for Half Quantum Numbers

If now we proceed on the new basis that the azimuthal quantum numbers can take the values $\frac{1}{2}$, $3/2$, $5/2$, . . . , or in general $n-\frac{1}{2}$, where $n=1, 2, 3$ . . . we may develop an elementary theory of quantization in space. If we assume in agreement with the work of Epstein[6] that the angular momentum of the molecule associated with the azimuthal quantum number, and the component of this angular momentum in the "specified" direction, can both be quantized, we may write for the azimuthal angular momentum,

$$p=(n-\tfrac{1}{2})h/2\pi \qquad (5)$$

and for the component momentum in the "specified" direction

$$p_\psi=(n_1-\tfrac{1}{2})h/2\pi \qquad (6)$$

where $(n-\frac{1}{2})$ is the azimuthal quantum number and $(n_1-\frac{1}{2})$ is the equatorial quantum number. The necessity of using half equatorial quantum numbers as well as half azimuthal quantum numbers arises from our acceptance of the hypothesis that quantum numbers can differ only by an integer combined with the hypothesis that the lowest

[6] Epstein, Ber. d. Phys. Ges. **19**, 116 (1917)

possible values for equatorial and azimuthal quantum numbers are the same.[7]

If α is the angle between the total angular momentum and the "specified" direction we may evidently write

$$\cos\alpha=\frac{p_\psi}{p}=\frac{n_1-\frac{1}{2}}{n-\frac{1}{2}}=\frac{2n_1-1}{2n-1} \tag{7}$$

Since n and n_1 must be integers greater than zero and $\cos\alpha$ must be less than unity, Eq. (7) imposes definite restrictions on the possible values of α. Giving n the successive value 1, 2, 3, . . . we can easily determine the possible values of α which are summarized in the following table.

		Number of values of α
Case I	$n=1;\ n_1=1;\ \cos\alpha=1$	1
Case II	$n=2;\ n_1=1;\ \cos\alpha=1/3$	2
	$n_1=2;\ \cos\alpha=1$	
Case III	$n=3;\ n_1=1;\ \cos\alpha=1/5$	3
	$n_1=2;\ \cos\alpha=3/5$	
	$n_1=3;\ \cos\alpha=1$	
Case IV	$n=4;\ n_1=1;\ \cos\alpha=1/7$	4
	$n_1=2;\ \cos\alpha=3/7$	
	$n_1=3;\ \cos\alpha=5/7$	
	$n_1=4;\ \cos\alpha=1$	

etc.

If we count positive and negative rotations separately, as is apparently required by the Bohr correspondence principle,[8] we may then write

$$p_n=2n \tag{8}$$

for the a priori probability of a state having the azimuthal quantum number

$$m=(n-\tfrac{1}{2}) \tag{9}$$

In connection with the above discussion of a priori probabilities, it should be noted how simply we have arrived at the conclusion that the a priori probabilities of the successive energy levels stand in the ratio 1, 2, 3, etc., without resorting to any artificial rejection of the states of no rotation or states where the plane of rotation is parallel to the specified direction.

[7] Compare Landé, Zeitschr. f. Phys. **11**, 357 (1922)

[8] Bohr, "On the Quantum Theory of Line-Spectra," Copenhagen Academy 1918, Part I, p. 25.

General Equation for Rotational Specific Heat

We may evidently write for the rotational heat capacity of one mol of an ideal diatomic gas consisting of molecules of the rigid "dumb-bell" model, the expression

$$C_R = N\frac{d}{dT}\left[\frac{\Sigma p_m e^{-m^2\sigma} m^2 kT\sigma}{\Sigma p_m e^{-m^2\sigma}}\right] \tag{10}$$

where, following Reiche[3] we have put

$$\sigma \equiv h^2/8\pi^2 JkT \tag{11}$$

and where N is the number of molecules in a gram-molecule, m is the azimuthal quantum number, J is the moment of inertia of the molecule, p_m is the a priori probability corresponding to m, and the summations are to be taken for all possible values of the azimuthal quantum number.

If now, following the procedure of Reiche[3] we write

$$Q = \Sigma p_m e^{-m^2\sigma} \tag{12}$$

it can readily be shown that Eq. (10) can be rewritten in the form

$$\frac{C_R}{R} = \sigma^2 \frac{d^2 \log Q}{d\sigma^2} \tag{13}$$

Using the a priori probabilities given by Eq. (8), corresponding to the quantum numbers given by (9) we may rewrite (12) for our case in the form

$$Q = \Sigma_1^\infty 2n e^{-(n-\frac{1}{2})^2\sigma} \tag{14}$$

Approximations for High, Low, and Intermediate Temperatures

At very *high* temperatures where σ is small we may evidently write the approximations

$$\begin{aligned} Q &= \int_0^\infty 2n e^{-(n-\frac{1}{2})^2\sigma} dn = \frac{1}{\sigma}[1+\tfrac{1}{2}\sqrt{(\pi\sigma)}]; \\ \log Q &= -\log\sigma + \tfrac{1}{2}\sqrt{(\pi\sigma)}; \\ C_R/R &= 1 - \sqrt{(\pi\sigma)}/8 \end{aligned} \tag{15}$$

and note that the value of C_R/R approaches unity as the temperature rises.

At very low temperatures where σ is large we may evidently write the approximations

$$\begin{aligned} Q &= 2e^{-\sigma/4}(1+2e^{-2\sigma}) \\ \log Q &= \log 2 - \tfrac{1}{4}\sigma + 2e^{-2\sigma} \\ C_R/R &= 8\sigma^2 e^{-2\sigma} \end{aligned} \tag{16}$$

At *intermediate* temperatures, we can generally obtain sufficient accuracy by considering the first four terms in Q. Eq. (13) can then be written

$$\frac{C_R}{R}=\sigma^2\frac{(1/16)e^{-\sigma/4}+(81/8)e^{-9\sigma/4}+(1875/16)e^{-25\sigma/4}+(2401/4)e^{-49\sigma/4}}{e^{-\sigma/4}+2e^{-9\sigma/4}+3e^{-25\sigma/4}+4e^{-49\sigma/4}}$$
$$-\sigma^2\frac{(1/4)e^{-\sigma/4}+(9/2)e^{-9\sigma/4}+(75/4)e^{-25\sigma/4}+49e^{-49\sigma/4}}{e^{-\sigma/4}+2e^{-9\sigma/4}+3e^{-25\sigma/4}+4e^{-49\sigma/4}} \qquad (17)$$

The Specific Heat Curve for Hydrogen

Making use of Eqs. (16) and (17) a number of values for C_R/R have been calculated for different values of σ, and are tabulated below. The temperatures in the third column are related to the values of σ by the equation

$$T=286/\sigma \qquad (18)$$

This corresponds to a value for the moment of inertia of the hydrogen molecule.

$$J=1.387\times10^{-41}\text{gm cm}^2 \qquad (19)$$

and gives the best correspondence between the experimental data and the calculated curve.

Table I

σ	$1/\sigma$	T	C_R/R
7	0.1429	40.9	0.000
6	0.1667	47.7	0.003
5	0.2	57.2	0.008
4	0.25	71.5	0.042
3⅕	0.3125	89.4	0.151
2⅜	0.375	107.3	0.270
2	0.5	143.0	0.533
1⅝	0.625	178.8	0.729
1⅛	0.75	214.5	0.813
1	1	286.0	0.845
⅕	1.25	357.7	0.852

Comparison with the Experimental Data and with the Curves of Reiche

The agreement between the calculated curve and the experimental values of Eucken and of Scheel and Heuse as cited by Reiche[3] is shown in Fig. 2. The full line is the best smooth curve through the calculated points, and the experimental points are indicated by crosses. The dotted lines give the upper portions of Reiche's curves Nos. III, IV and V. At low temperatures these curves of Reiche are in as satisfactory agreement as our own with the experimental points. At the higher temperatures none of the curves agree with all the experimental points.

Reiche's calculations employing different assumptions as to the form of Q may now be compared with the calculations made in this paper.

(I) $$Q=\Sigma_0^{\infty}(2m+1)e^{-m^2\sigma}.$$

This form for Q is obtained on the assumption that the lowest possible azimuthal quantum number is zero, and that positive and negative rotations are to be counted twice in determining a priori probabilities. It leads to a specific heat curve with a maximum value for C_R/R at low temperatures and cannot agree with the experimental facts.

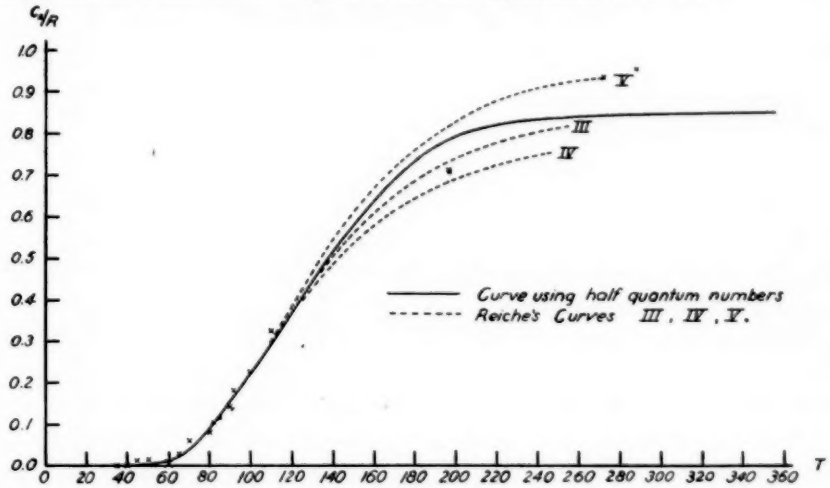

Fig. 2

(II) $$Q=\Sigma_0^{\infty}(m+1)e^{-m^2\sigma}.$$

This form for Q is obtained on the same assumptions as above except that positive and negative rotations are only counted once in determining a priori probabilities, a procedure, however, which is apparently not in agreement with the correspondence principle. It also leads to an impossible specific heat curve with a maximum value for C_R/R at low temperatures.

(III) $$Q=\Sigma_1^{\infty}(2m+1)e^{-m^2\sigma}.$$

This form for Q is obtained by counting positive and negative rotations twice, but excluding the possibility of no rotation. With the value for the moment of inertia $J=2.214\text{x}10^{-41}$ it agrees with the experimental points at low temperatures but fails at high temperatures.

(IV) $$Q=\Sigma_1^{\infty}(m+1)e^{-m^2\sigma}.$$

This form for Q is obtained on the same assumptions as for (III) but counting positive and negative rotations only once. With the value for the moment of inertia $J=2.293\text{x}10^{-41}$, it agrees with the experimental points at low temperatures but fails at high temperatures.

(V) $$Q=\Sigma_1^{\infty}\ 2me^{-m^2\sigma}.$$

This form for Q is obtained on the same assumption as for (I) but ex-

cludes not only the case of no rotation but somewhat arbitrarily all cases where the plane of rotation is parallel to the specified direction. With the value $J=2.095\times10^{-41}$ it agrees with experimental points at low temperatures and with the two points at the highest temperatures but fails to agree with the points at 197°.

(VI) $$Q=\Sigma_0^\infty(2n+1)e^{-(n^2+n+\frac{1}{2})\sigma}.$$

This form for Q is based on calculations made by Planck, using the second form of quantum theory. It leads to a specific heat curve with a maximum 10 per cent greater than the classical value and cannot agree with the experimental facts.

(VII) $$Q=\Sigma_1^\infty 2ne^{-(n-\frac{1}{2})^2\sigma}.$$

This is the form for Q discussed in this paper. It takes the lowest possible azimuthal quantum number as one half and makes no arbitrary exclusions in determining the a priori probabilities. With the value for the moment of inertia $J=1.387\times10^{-41}$ it agrees with the experimental data at low temperatures as well as any curve of Reiche's. This lower value for the moment of inertia is of interest since Sommerfeld[9] concludes from the many lined spectrum of hydrogen that the moment of inertia of an excited hydrogen molecule is 1.9×10^{-41}, and the moment of inertia of the unexcited molecules involved in determining specific heats at low temperatures must be lower than that figure, a condition which is met by the new curve and not by those of Reiche. The failure of all the curves at the higher temperatures may be due to the over simplification involved in assuming the rigid "dumb-bell" model for the hydrogen molecule, which can at best be regarded only as a first approximation.[10]

The assumption of half quantum numbers has also been used for calculating the entropies of diatomic gases and shown to agree as well with the experimental facts as any of the older assumptions.[11]

In conclusion the writer wishes to express his appreciation to Professors Charles G. Darwin and Paul S. Epstein for very helpful suggestions and criticisms.

NORMAN BRIDGE LABORATORY OF PHYSICS,
PASADENA, CALIFORNIA,
May 16, 1923.

[9] Sommerfeld, "Atombau und Spektrallinien," 3rd edition, page 535, Braunschweig 1922. It should be noted that the change to half quantum numbers does not affect the relation $\Delta\nu=h/4\pi^2J$ for the spacing between lines.

[10] At high enough temperatures, an appreciable amount of energy of oscillation may enter in. See the treatment of Kemble and Van Vleck, Phys. Rev. **21**, 653, 1923, which has appeared since the above was written.

[11] See Tolman and Badger, J. Amer. Chem. Soc. **45**, 2277, 1923.

THE FREE ELECTRON CHARACTERISTICS OF SODIUM-POTASSIUM ALLOYS

By C. V. Kent

Abstract

Simple electron theory of sodium-potassium alloys.—(1) *The impact frequency and density of free electrons calculated from the optical data* of Morgan are given. The chief source of uncertainty is the determination of the effect of the bound electrons on the optical constants. The number of free electrons per atom is found to be about 1.5 for all the alloys, but with indication of a minimum of about 1.2 for the $\frac{1}{3}$ sodium alloy. The frequency of impact of a free electron with molecules comes out from 1 to 3×10^{14}, less than the frequencies found for the metals lead, tin, bismuth, cadmium, and mercury, previously investigated by the author. The impact frequency increases linearly with increase in percent of either constituent to a maximum for the compound NaK supposed to exist in these liquid alloys. (2) *The resistivities calculated from the optical constants* agree with experimental data for the pure liquid metals and for two alloys within the limits of error. The variation of resistivity with composition is compared with values for Na-K alloys at 200° C. These results tend to show that the simple Drudean optical theory holds for liquid alloys which form compounds as well as for those which do not.

SOME time ago the writer[1] investigated the optical constants of liquid alloys of lead with bismuth, tin, cadmium and mercury, in which compounds are not formed. Assuming the simple electron theory of Drude, it was shown that the number of impacts per second of a free electron with molecules (and ions), and the number of free electrons per cm^3, were both linear functions of the atomic concentration, as might be expected, and that contrary to the case with the solid metals, the electrical resistivities can be calculated from the optical constants. Thus the simple electron theory seems applicable *as a working basis* in dealing with liquid metals.

Last year, Morgan[2] published experimental determinations of the optical constants of liquid sodium-potassium alloys at temperatures below 100° C. These have been used to calculate the free electron parameters of the Na-K alloys, thereby testing the validity of the extension of the theory to other liquid metals.

[1] C. V. Kent, Phys. Rev. **14,** 459, Dec. 1919
[2] W. Morgan, Phys. Rev. **20,** 204, September 1922

Method of Determining Free Electron Characteristics

The formulas are discussed in the writer's original paper. With a slight modification in terminology, they are:

$$\nu^2-\kappa^2=X=A-4\pi\frac{Ne^2/m}{\omega^2+W^2} \tag{1}$$

$$2\nu\kappa=Y=B+4\pi\frac{W}{\omega}\,\frac{Ne^2/m}{\omega^2+W^2}. \tag{2}$$

$\nu^2-\kappa^2$ and $2\nu\kappa$ correspond to $n^2(1-k^2)$ and $2n^2k$ in the terminology of Morgan's paper. A and B are terms expressing the effect of the bound electrons, i. e., they are the values of $\nu^2-\kappa^2$ and $2\nu\kappa$ for the molecules (and ions) of the metals. The fractions on the right in each equation are due wholly to the free electrons; ω is equal to $2\pi n$, where n is the frequency of the light used; e and m are the charge and mass, respectively, of the electron; N is the number of free electrons per cm^3, and W is one-half the average number of impacts per second of a free electron with molecules or ions. N and W are the free electron parameters which are to be determined for the different metals.

From Eqs. (1) and (2),

$$W=-\omega\frac{Y-B}{X-A} \tag{3}$$

$$N=-\frac{\omega^2m}{4\pi e^2}\,\frac{(X-A)^2+(Y-B)^2}{X-A} \tag{4}$$

The electrical resistance for constant current is given as $\rho=mW/Ne^2$. Therefore, from (3) and (4)

$$\rho=\frac{4\pi}{\omega}\,\frac{Y-B}{(X-A)^2+(Y-B)^2} \tag{5}$$

In the previous paper the sign between the parentheses in the equations at the top of page 486, corresponding to (4) and (5) above, was printed incorrectly as minus.

A glance at Table I will show that Y^2 is less than 1 per cent of $(X-A)^2$ in all cases and $(Y-B)^2$ may therefore be neglected. B will be omitted, for reasons given later. The following approximate formulas are therefore allowable for these metals and alloys:

$$W=-\omega\frac{Y}{X-A} \tag{6}$$

$$N=-\frac{\omega^2m}{4\pi e^2}(X-A) \tag{7}$$

$$\rho=\frac{4\pi}{\omega}\,\frac{Y}{(X-A)^2} \tag{8}$$

To evaluate the bound electron parameters A and B, the optical constants of the non-conducting portions of the metals must be known. They are usually assumed to be of the same size as for ordinary insulators. If the optical constants of the metal in question have been determined throughout the visible spectrum, it is generally possible to obtain an approximate idea of their sizes, as has been done by W. Meier[3] and others for solid metals. The primary factor fixing the optical constants of insulators is resonance frequency. In the previous work it was assumed that no new selective absorption or large change in that already present in solid metals, at least near the visible spectrum, was produced by fusion. Fortunately selective absorption seemed to be absent near the visible spectrum in every case, so κ for the non-conducting portion was equal to zero. ν^2 and hence A ($\nu^2-\kappa^2$ for the non-conducting part) were taken as equal to 2.5, following Schuster.[4] Drude takes 3. Since for the alloys of lead with bismuth, tin, cadmium and mercury, $\nu^2-\kappa^2$ varied between -8 and -25, A could be assumed of any value within wide limits without seriously affecting N, W, and ρ.

It is just at this point, however, that the greatest difficulty and uncertainty lie in the present work. X varies from -8 for pure sodium to -1.8 for potassium, and incorrect assumptions as to the magnitudes of A and B are somewhat serious. Information which might be of help is meager. Morgan's work is all that is available for the liquid state, and that for only one wave-length.

The most complete set of data at hand for these solid metals is that of R. W. and R. C. Duncan,[5] giving the constants of sodium for five wave-lengths, and of potassium for three. The wave-lengths used are insufficient in number, and the differences between observations of successive surfaces are somewhat large. No certain information can be gained from the $\nu^2-\kappa^2$ curves. The $2\nu\kappa$ curves, however, seem to show an abnormal rise in absorption for the shorter wave-lengths. This may be more easily seen if $2\nu\kappa$ is plotted against λ^3. (Table I shows that W^2 is small compared with ω^2; neglecting it, Eq. (2) becomes $Y=B+4\pi Ne^2W/m\omega^2$.) Whatever may be the optical formulas applicable to solid metals, the evidence indicates that they will be substantially of the form of (1) or (2). Therefore Y, λ^3 curves for the solid metals should be straight lines passing through the origin, when absorption is absent. These graphs indicate selective absorption in the violet end of the visible spectrum in the case of sodium, and that there is

[3] W. Meier, Ann. der Phys. **31**, 1035, 1910
[4] W. Schuster, Phil. Mag. **7**, 151, 1906
[5] R. W. and R. C. Duncan, Phys. Rev. **1**, p. 294, 1913

probably absorption present nearer to the light used by Morgan (5460 A) for potassium. The writer believes that Duncan's assumption of possible selective absorption for sodium at 5890 A needs further careful work for its substantiation.

The data we have are inconclusive but may point to selective absorption for both metals on the violet side of the working wave-length (5460 A). This means a relatively high value of A. The writer has therefore assumed the value to be 3 or 4 and admitted a possible appreciable magnitude for B in the case of potassium and alloys high in this component. Owing to the neglect of this B term in the numerical calculations, W and ρ will be too large, especially for potassium and the alloys rich in this metal.

The optical constants of pure sodium were determined by Morgan for the solid state only, and cannot be used here. However, since the alloys of the previous investigation showed a smooth variation of the optical constants with atomic concentration, $\nu^2-\kappa^2$ and $2\nu\kappa$ were plotted against atomic concentration for the Na-K alloys containing 32.5, 25.1, and 11 atomic per cent potassium. $\nu^2-\kappa^2$ and $2\nu\kappa$ were then found by extrapolation to be -6.8 and .35 respectively for liquid sodium. They are -4.94 and .209 for the solid. Only the observations for 75° C were used for pure potassium, the others being below the melting point. The electron parameters have been calculated for both $A=3$ and $A=4$.

TABLE I

Atomic percent K	0	11	25.1	32.5	41.8	53.3	62.7	76	100.
$-(\nu^2-\kappa^2)$.....	6.8	4.85	3.41	3.18	3.21	2.91	2.50	2.39	1.81
$2\nu\kappa$.....	.35	.357	.370	.392	.413	.469	.394	.273	.163
$A=3$									
$N\times10^{-22}$.....	3.67	2.94	2.40	2.31	2.32	2.21	2.06	2.02	1.80
Free electrons per atom.....	1.50	1.33	1.21	1.23	1.31	1.33	1.33	1.39	1.40
$W\times10^{-14}$.....	1.25	1.59	2.02	2.22	2.33	2.78	2.51	1.93	1.12
$A=4$									
$N\times10^{-22}$.....	4.05	3.31	2.77	2.68	2.70	2.59	2.44	2.41	2.17
Free electrons per atom.....	1.66	1.50	1.40	1.43	1.52	1.56	1.56	1.65	1.69
$W\times10^{-14}$.....	1.05	1.41	1.75	1.91	2.00	2.38	2.12	1.63	0.92

The results are plotted in Fig. 1. While the absolute magnitudes of these parameters are somewhat uncertain, their relative values show little variation with change of A.

Within the limits of error, the number of free electrons per atom is 1.5, although the work is not precise enough to establish an integral number of free-electrons-per-molecule ratio such as seems to have been

indicated with the metals previously examined. The number per atom is practically constant, however, except for a small decrease on the Na side of the diagram whose maximum drop of nearly one third per atom occurs at a composition of about one third potassium. This corresponds to the position of the unstable compound Na_2K known to exist in the solid but "dissociating below its melting point."[6] The variation is too large to be ascribed to experimental error. It is possible that the tendency to form Na_2K still persists in the liquid, resulting in an absorption of free electrons such as takes place in the formation of metallic salts, or the potassium atoms may possess an affinity for

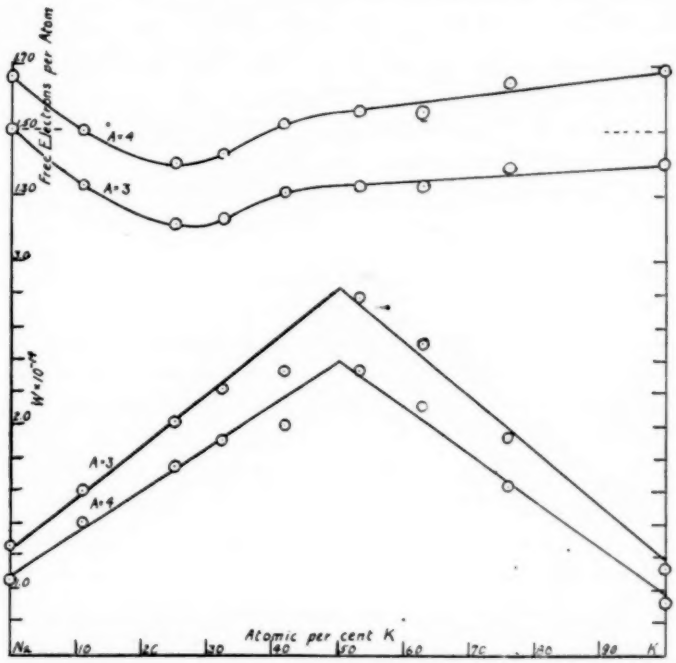

Fig. 1

electrons which is superior to that of sodium. In fact, some such difference in affinity may be the explanation of the drop in electron density for dilute solutions of cadmium and of tin in lead which were noticed in the previous work. Whatever the cause, there is a "recall" of about one free electron for each system, 2Na+K.

The free electron impact frequencies of these metals is seen to be very low in comparison with those of the metals previously studied, indicating

[6] C. H. Desch, "Intermetallic Compounds," Longmans, Green and Co., p. 92

a relatively small "impact area" of the atoms. Their good electrical conductivity is due primarily to this low impact frequency.

As shown in the figure, the frequency increases linearly with the atomic per cent of either metal, the two straight lines meeting at the composition NaK, the compound supposed to exist in these liquid alloys. If it does exist, and this work seems to confirm the suggestion, the sodium and potassium atoms unite without associating any of the free electrons with themselves. This is a result quite unexpected by the writer. The sole effect of the combination is to increase the "total area" of impact of the atoms to more than two-fold. This may be inconsistent with the conception of the "impact" of the older theories. The writer believes that he has sufficient evidence (not yet in publishable form) to show that the "impact" of a free electron with an atom or a molecule is of a quite different type from that usually assumed.

If the optical data for these metals are consistent, they should give values of the electrical resistivities within experimental error. The results of these calculations are given in Table II, together with electrical resistivities given by various recent authorities, and similar data for the solid metals.

TABLE II

Resistivity in microhms as function of atomic per cent K.

Atomic percent K	0.0	11.0	25.1	32.5	41.8	53.3	62.7	76.0	100
From opt. data:									
($A=3$).....	12.0	19.0	29.5	33.6	35.1	44.0	42.6	38.2	21.7
($A=4$).....	9.8	15.0	22.0	24.9	26.1	32.2	30.5	27.2	14.9
From elec. data:.	9.7[7]	....	.....	33.8[7]	.....	35.0[8]	.....	.....	14.9[7]
Solid									
From opt. data:[2]									
($A=3$).....	10.9	.....	.....	.....	.....	.....	.....	.....	27.3
($A=4$).....	8.6	.....	.....	.....	.....	.....	.....	.....	16.5
From elec. data:									
(20° C).....	5.	.....	.....	.....	.....	.....	.....	.....	7.

The agreement between electrical and optical data is as good as could be expected. The omission of a possible selective absorption (i. e., the term B) for potassium gives unduly high "optical" resistivities of alloys rich in potassium. The non-linearity of the change in resistivity with composition is seen to be due primarily, according to this theory, to changes in impact frequency.

[7] E. F. Northrup, Trans. Am. Electro-Chem. Soc. **20,** 185, 1911. The resistance of potassium is reduced to 75° C. He gives the resistivity of an equal volume alloy with about 34 per cent (atomic) of potassium.

[8] J. W. Hornbeck, Phys. Rev. **2,** 217, 1913

Kraus[9] gives the conductivities of various alloys of sodium and potassium at 200° C. In Fig. 2 the resistivities of these alloys have been plotted in comparison with those computed from optical data in this work at an approximate temperature of 75° C. A is taken as equal to 4. The drop in the resistivity at about one third potassium, which existed at the lower temperature, has vanished at 200° C. This is to be expected, if the tendency toward the formation of Na_2K is the explanation of the decrease in the number of free electrons per atom

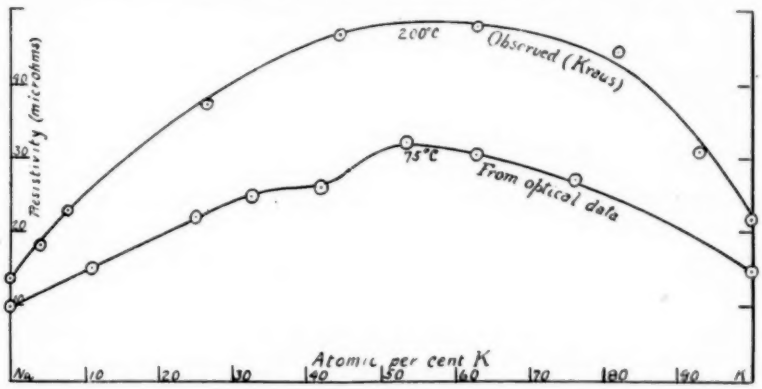

Fig. 2

at this point. In addition, the fairly sharp maximum at 50 atomic per cent K has been much rounded off, due, no doubt, to partial dissociation of the compound NaK.

The optical examination of liquid alloys gives results very much less precise than those found by electrical experimentation. On the other hand, *if the present electron theory is a valid working basis* for the interpretation of the behaviour of liquid metals, it allows the evaluation of the *two* free electron parameters necessary to determine the action of these electrons in the metal. As far as the writer is aware, this has not been done quantitatively by purely electrical methods.

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March 7, 1923.

[9] C. A. Kraus, "The Properties of Electrically Conducting Systems," Chem. Cat. Co., p. 398

THE EFFECT OF CRYSTAL STRUCTURE ON MAGNETOSTRICTION

By C. W. Heaps

Abstract

Magnetostriction of steel, soft iron, and magnetite was investigated, using a Weiss electromagnet to produce the field, whose strength was varied up to 10,000 or 20,000 gauss depending on the specimen and an apparatus of the lever type for measuring dimension changes to within about $2(10)^{-7}$cm. Curves are given showing the behavior of a steel sphere, both before and after annealing. A sphere of soft Norway iron gave larger effects than the steel sphere, effects which varied with the orientation of the sphere in the field. A soft iron disk, part of a single grain formed in a plate of iron with 3½ per cent Si, showed larger dimension changes than have yet been found in iron. *Along different diameters* of the disk quite different results were obtained; in some cases there was a contraction, in others, an expansion. Preliminary work with a magnetite sphere, 1.43 cm in diameter, indicated a lack of cubic symmetry for both the transverse and longitudinal effects. Changing the direction of the field with respect to the crystal axes may change the magnetostriction in a given direction from a contraction to an expansion; also transverse magnetostriction, with a fixed direction of magnetic field, is a contraction for some directions in the crystal, an expansion for others. *Theories* are briefly discussed. It is suggested that the ordinary magnetostriction curve of iron is the resultant of two or more different types of curves which are characteristic of the small individual crystals in different orientations, the composite curve depending on the heterogeneous arrangement of the crystals. The experiments suggest that the Villari reversal is also probably a consequence of heterogeneous crystal arrangement in the iron. Ewing's latest model of the magnetic atom seems to be capable of explaining the various magnetostrictive effects.

WHEN a bar of iron is placed with its length parallel with a continually increasing magnetic field, numerous experiments have shown that its length changes in the following way. The bar first grows longer, then contracts to its original length, and as the field increases continues to contract. In a few cases it has been found that there is no initial lengthening of the bar,[1,2] contraction resulting even in the smallest fields. It has been suggested that this failure to observe an initial lengthening is the result of insufficiently sensitive measuring apparatus. However that may be, there is no doubt but that some specimens show a much smaller initial lengthening than do others. Rhoades has found[3] that the fibrous structure of the specimen exerts a marked influence on its magnetostriction. Heat treatment is also important in determining the nature of the magnetostriction curves.

[1] Bidwell, Proc. Roy. Soc. **55**, 228, 1894
[2] Heaps, Phys. Rev. **6**, 34, 1915
[3] Rhoades, Phys. Rev. **7**, 66, 1898

These facts seem to indicate very clearly that the crystal structure of the specimen is of considerable importance in determining the form of its magnetostriction curves and a knowledge of this crystal structure is of prime importance. A bar or wire of metal must be considered as æolotropic because it is improbable that the small crystals composing the specimen would completely retain their random orientations after the drawing or rolling process. The degree of æolotropy would depend on the mechanical treatment given the specimen so that it is not surprising that results obtained with different specimens are sometimes discordant.

The somewhat complicated behavior of iron in this respect suggests that the ordinary magnetostriction curve might be considered as the resultant of two curves, one of which would represent an expansion to a constant maximum value, the other a contraction which possibly approaches a constant value as the field increases. Suppose that when all the small crystals of the iron are oriented so as to have a certain crystallographic axis parallel with the field one of these types of curves is obtained, and when they are oriented so that all have a different axis parallel with the field the second type of curve is obtained; then for a random orientation of the crystals we should expect the resultant curve. If this view is correct, theories of magnetostriction would require considerable modification in order to explain these two curves. Actually there is no theory at present which is generally satisfactory, a fact which is not at all surprising in view of the unsettled character of our theories of ferro-magnetism.

Some experiments made on various kinds of iron and on some natural crystals of magnetite have given very different types of curves with the same specimen when magnetized in different directions. These results lend support to the hypothesis of the existence of two types of curves. It is possible, however, that the single iron crystal may give even more than these two types.

APPARATUS

For the purpose of this experiment it was necessary to measure the magnetostriction of a specimen for various orientations with respect to the magnetic field. For this reason wherever possible a sphere was the form chosen. Another advantage of this form is that an isotropic sphere is magnetized uniformly when in a uniform field, hence there are no distortions produced by the elastic transfer of stresses resulting from unequal dilatations of various parts of the same specimen. The sphere, however, has a large demagnetization factor so that a strong magnetic

field is necessary in order to obtain the proper intensity of magnetization. Partly for this reason a large Weiss electromagnet with pole-pieces 10 cm in diameter and 4.65 cm apart, was used. The field, therefore, could be considered as only approximately uniform but this disadvantage seemed less than the disadvantages of using the weaker and more inaccessible field of a solenoid.

The specimens used were necessarily small. It was important, therefore, to construct a measuring device of high sensitivity. A lever system was used. In Fig. 1 (I) the sphere G is shown pressed by means of the spring C into a small depression in the brass plate A. The sliding cross-

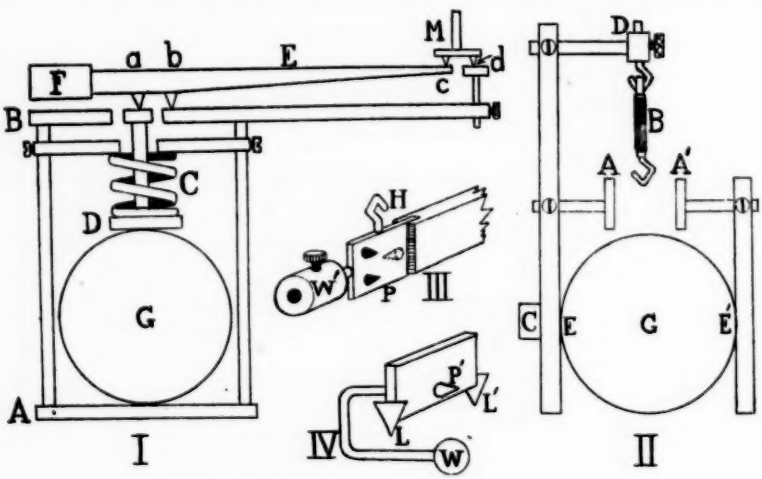

Fig. 1. Apparatus

bar pressing down on top of the spring serves to regulate this pressure. A depression in the brass plate D enables the sphere to be held more rigidly, and carborundum powder ground into these depressions in A and D facilitate the clamping. The brass post fixed vertically in the center of D passes through a hole in the plate B and has a glass plate fixed with sealing wax across its top. The lever E is made of wood, the counter-weight F of brass. The bearing point at a is a short conical glass rod with a tiny spherical tip; the bearing under b is an agate knife edge taken from a chemical balance, and rests on a glass bearing surface. The legs of the mirror M are made of small, conical glass rods with spherical tips from 0.01 to 0.02 cm in diameter, and they rest on glass plates at c and d.

The instrument is placed between the poles of the magnet with the lever E horizontal and at right angles to the field. The supporting stand, not shown in the diagram, consists of a heavy, solid brass cylinder set

on end and bearing two screws between which the sphere is clamped. These screws press against opposite ends of a diameter through G perpendicular to the plane of the drawing. With this method of support it is seen that the entire apparatus for detecting dimension changes is fixed to the sphere itself, so that any small motion of the sphere as a whole will not introduce large errors.

No iron is used anywhere in the measuring device. The dimensions of the lever system were as follows: $ab = 0.31$ cm, $bc = 31.7$ cm, $cd = 0.184$ cm. The image of a lamp filament was reflected from M upon a scale which during most of the experiments was 365 cm distant. The magnifying power is therefore calculated to be 405,700.

The instrument shown in Fig. 1 (I) is capable of making measurements only of dimension changes perpendicular to the field. To measure the longitudinal effect, that is, the dimension changes parallel to the field, the apparatus shown in Fig. 1 (II), (III) and (IV) was constructed. Referring to (II), two vertical wooden bars were fixed to the ball at E and E', either by the use of de Khotinsky cement or by means of small brass screws threaded into the ball. A and A' are two glass plates, the distance apart of which may be easily altered. B is a rubber cord supplied with hooks as shown. At C is fixed a long wooden arm extending out perpendicular to the plane of the drawing and carrying at its end a small adjustable glass platform like that shown in (I) under d. The weight of this arm was counterbalanced by an extension backward to the other side of C. In (III) is shown a section of the lever used here. A hook H and a counterweight W' are fixed to the glass plate P. Glass bearing points are fixed with sealing wax to this plate as shown, one of the points being supposed visible through the plate. These bearing points were made as short as possible in order to secure greater strength. The spherical tips were from 0.01 to 0.02 cm in diameter. This lever was hung by the hook H to the bottom end of the rubber cord B, the plates A and A' were adjusted against the glass bearing points, and the rod D turned about a vertical axis till the pressure of the bearing points against the glass plates was sufficient to hold the lever in a very stable position. The end of the lever not shown in the diagram carried a small glass plate with its plane vertical. This plate was designed to press against the glass bearing point P' fixed to the mirror of diagram (IV). The legs L and L' of this mirror were triangular pieces of glass chipped from a thin cover glass. The points were very sharp. The counterweight W was sealing wax stuck to the bent glass rod as shown. This mirror stood on the glass plate at the end of the arm C, the line LL' being parallel to the length of the arm. The weight W was adjusted

so that the mirror was in equilibrium on its two legs but leaned forward quite appreciably. The plate on the end of the lever shown in (III) by pressing against the point P' held the mirror so that its plane was approximately vertical. Any motion of the end of the lever arm would thus alter the tilt of the mirror. To prevent slipping the surface of the glass platform carrying the mirror was ground with fine carborundum; in fact it was found advantageous to grind in this way all of the glass plates used in the apparatus as bearing surfaces. The sphere under test was supported between screws at G just as in the first apparatus, but the support was turned so that the magnetic field was parallel to the line joining EE'. The magnifying power of this system was about the same as that of the one shown in (I).

The magnetic induction through the specimen was measured by means of a carefully calibrated fluxmeter connected to several turns of wire wrapped around the sphere. The sphere was placed between the poles of the magnet and the fluxmeter deflections noted when the exciting current was turned on or off. The effect of the residual field of the magnet was thus neglected. It amounted to about 35 gauss.

Sources of Error

One of the chief sources of error lay in the non-uniformity of the magnetic field. When an iron sphere was placed between the poles of the magnet quite a strong force acted upon it unless it was very carefully centered between the two pole-pieces. This force was always made as small as possible by careful adjustment but it was probably always present in some degree. This force on the ball was resisted by the pressure of the screws supporting the ball, hence distortions of a nature not desired in this experiment would arise. However, it was concluded that such distortions were small compared with other magnetostrictive effects for the following reason. When the sphere was properly centered no motion of the ball or its support could be detected when the magnet was excited, though of course the mirror was slightly tilted by the magnetostriction of the ball. With the exciting current off pressure was applied to one side of the ball till a slight motion of the support could be detected. The spot of light reflected from the mirror vibrated violently under these conditions but its rest position appeared to be unchanged. The resulting dimension change must, therefore, have been too small to shift the zero position of the mirror.

Another source of error might lie in the magnetic traction on various light movable parts of the apparatus. No iron was used in the construction but it seems possible that some effect of this kind was present.

When a ring of brass was substituted for the ferromagnetic sphere the largest magnetic field used produced a deflection of the spot of light of about 1 mm. The cause of this deflection might have been a contraction of the brass ring, a tilting of the support due to some slight motion of the base of the magnet, or a direct action of the non-uniform field on the lever system. This error was not eliminated. In most cases it was small compared with the observed deflection.

The pressure of the screws holding the specimen could not be adjusted to have always the same value, hence in general there would not be the same magnetostriction effect after a readjustment of the specimen because the magnitude of magnetostriction depends on the state of strain of the specimen. This source of error is probably too small to be important.

Temperature changes of the specimen caused a slow drift of the spot of light. However it was not difficult to separate this temperature effect from the magnetostrictive effect. Readings were taken rapidly to minimize this error. There was always an irregular motion of the spot of light, sometimes amounting to a slight blurring of the image, because of vibrations of the building. By choosing quiet hours of the day these vibrations were made small enough to cause little trouble.

When cement was used at E and E', Fig. 1 (II), there frequently existed a steady and fairly rapid drift of the zero point on the scale. This was caused by a viscous yielding of the cement. In only one instance was a satisfactory curve obtained under these conditions. Where possible brass screws were used to fix the supports to the ball; in the case of magnetite the sphere was fitted into depressions in the supports and the supports held firmly by rubber bands passing around the ball and the two supports. Carborundum powder at E and E' prevented slipping.

The apparatus gave reproducible results, a condition which has not always been realizable with this type of apparatus.[4] The bearing points L and L' did not slip on the ground glass surface. Such a slipping would have been indicated by a characteristic displacement of the zero after any motion of the mirror.

Results

The first experiments were made on a steel ball of diameter 1.9 cm, and only the dimension change perpendicular to the magnetic field was measured for this specimen. Fig. 2 shows the curves obtained with this ball before and after annealing. The change of diameter per cm (dL/L) is plotted against the magnetic induction B. The diameter

[4] Rhoades, Phil Mag. **2**, 468, 1901

transverse to the field is seen to decrease for the fields used and annealing has increased this contraction effect. The arrows beside the curves indicate whether the field was increasing or decreasing when the respective curves were obtained. Hysteresis is peculiar in that the ball continues to contract as the field is decreased from the maximum value till its diameter is smaller than anything obtained with the increasing field. These results are in qualitative agreement with most of the work of previous experimenters. Bidwell, it is true, has found annealing to decrease the magnitude of the effect in one specimen but this result seems to be an exception to the general rule. Nagaoka[5] and others

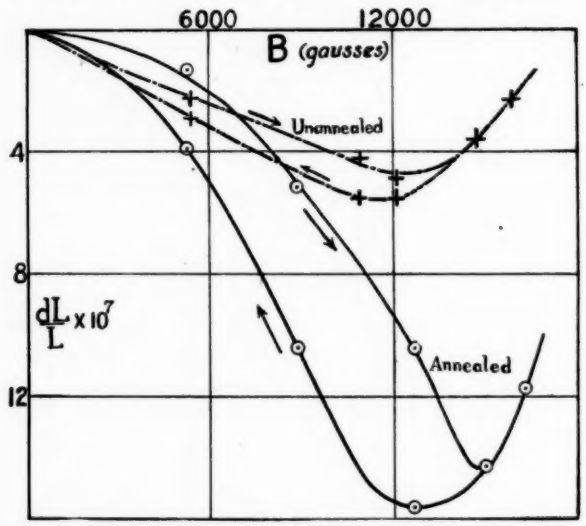

Fig. 2. Magnetostriction for steel ball, perpendicular to the field

have found the return curve of the hysteresis loop crossing the initial curve. Possibly insensitiveness of the apparatus has prevented this phenomenon from showing in the curves of Fig. 2. Rhoades, however, did not observe this crossing in most of his specimens. Self-demagnetization of the sphere was so great that the sphere returned approximately to its original dimensions when the magnetizing current was cut off. By using the fluxmeter it was found that the intensity of magnetization remaining in the annealed sphere after a cycle had been performed was less than 15 units.

The next sphere examined was turned from a cylindrical bar of soft Swedish iron. Its diameter was 1.46 cm. Curves *A* and *B*, Fig. 3, show how the transverse contraction of the sphere varies with the induction through the sphere. For curve *B* the contraction was measured

[5] Nagaoka, Phil. Mag. **37**, 131, 1894

along the axis of the ball (the axis being defined as the direction parallel with the axis of the original bar from which the ball was turned), the magnetic field being perpendicular to this direction. For *A* the field was parallel to the axis, the contraction perpendicular to this direction. The circles near curve *A* are observations made when both the contraction and the magnetic field were perpendicular to the axis. Curves *C* and *D* represent expansions in the direction of the field. For *C* the axis of the ball was parallel with the field, for *D* it was perpendicular to the field.

These curves show that the maximum longitudinal expansions and transverse contractions are of the same order of magnitude. It is of interest to note that according to these curves the volume of the sphere

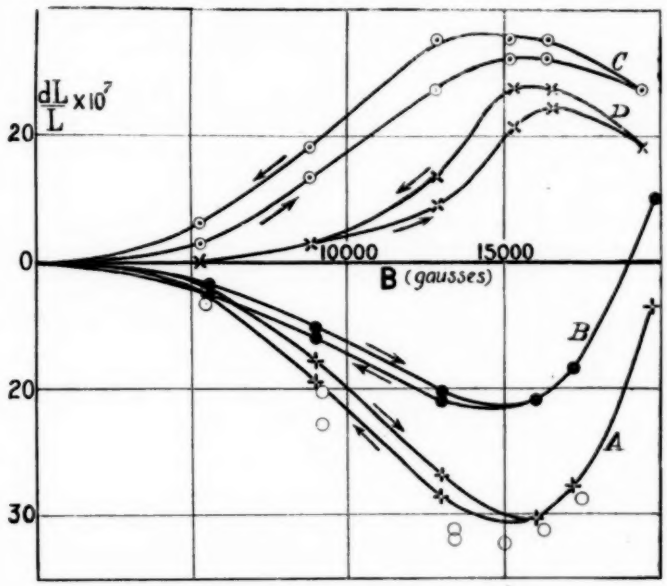

Fig. 3. Results for soft Swedish iron.
A and B transverse effect; C and D longitudinal effect

is first diminished then increased as the induction increases. Calculation shows that the longitudinal elongation must exceed twice the transverse contraction before the volume of the sphere is increased by the magnetization, and this condition is not realized till the induction is around 17,000. Nagaoka and Honda[6] have found the volume of an iron ovoid to increase continually in a longitudinal field. Bidwell observed the dimension changes of an iron ring and concluded that the volume of the ring was decreased by magnetization. These con-

[6] Nagaoka and Houda, Phil. Mag. **46**, 261, 1898

tradictory results may be explained by differences in the nature of the iron used.

The curves of Fig. 3 corroborate the work of Rhoades and others in demonstrating the effect of fibrous structure on the magnetostriction curve of iron. It seems probable, however, that the mechanical treatment of the bar during its fabrication has not succeeded in producing any very great lining up of the elementary crystals of the iron; the magnetostriction curves for different orientations of the sphere are too similar. Furthermore, the induction in the specimen seemed to be independent of its orientation in the field.

A crystal of magnetite, an octahedron, was next ground into a sphere of diameter 1.43 cm. This sphere had a few pits in it but on the whole was satisfactory. Though belonging to the cubic system this crystal showed a tendency to split along a certain direction. In other words, there was one plane perpendicular to one of the four trigonal symmetry axes of the crystal which favored cleavage more than any other. When placed in the magnetic field the induction in this sphere, measured as described above, was found to be independent of the orientation of the sphere. A more sensitive apparatus might have detected differences, for Quittner[7] has investigated magnetite and found the magnetic properties varying in a complicated way for different directions and different field strengths. The magnetostriction of this sphere was studied for a number of different positions of the crystal. Curves similar to those of Fig. 4 were obtained, and the orientation of the crystal was found to be an important factor in determining the form of the curve. Hysteresis effects were smaller than in the case of iron so are not shown in the curves, which give results for an increasing field. For some positions of the sphere curves were obtained which were not like those of Fig. 4, but they could have been produced by a combination of the types there shown. The two continuous curves of Fig. 4 represent the magnetostriction transverse to the field for two different settings. These particular curves are reproduced because they show respectively the maximum contraction and maximum elongation observed in directions perpendicular to the field. The contraction curve (plotted below the B axis) was obtained with the field making an angle of 45° with that crystal axis which is perpendicular to the plane of easy cleavage. It is not known whether the field in this case was parallel to a tetragonal axis, though such might have been the case. The contraction was measured normal to the plane determined by the magnetic field and the

[7] Quittner, Ann. der Phys. **30**, 289, 1909

above-mentioned trigonal axis which is perpendicular to the plane of easy cleavage.

The expansion curve (the continuous line plotted above the B axis) was obtained when the sphere was arranged just as above except that the magnetic field had been turned through 90° about the diameter of the magnetite sphere. Simply changing the direction of the magnetic field with respect to the crystal axes has sufficed, therefore, to convert its effect along a given perpendicular direction from a contraction to an expansion.

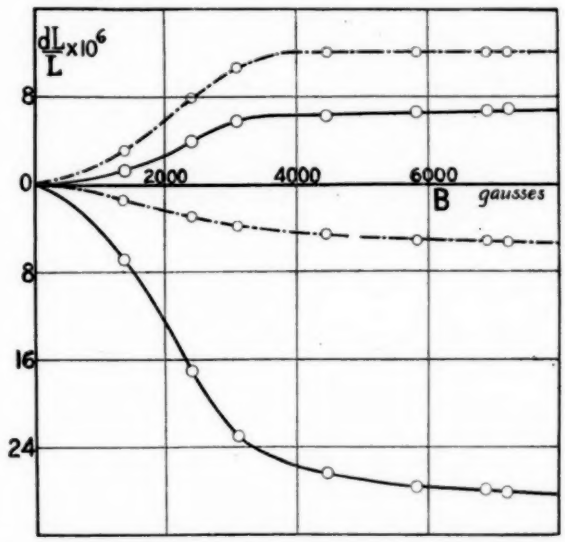

Fig. 4. Curves for various positions of a spherical magnetite crystal

If the direction of the magnetic field is kept constant and the sphere rotated about this direction as an axis the magnetostriction in different directions perpendicular to the field may be observed. In this case an angular displacement of 90° was found to convert a contraction into an expansion.

The dotted curves of Fig. 4 represent magnetostriction in the direction of the magnetic field. The expansion curve, above the B axis, was obtained along a trigonal symmetry axis; the contraction curve, below the B axis, was obtained with the field in one of the principal planes of symmetry of the crystal.

These curves for magnetite show the vital importance of crystal structure in relation to magnetostriction. A more detailed investigation of the relation of the crystalline axes to the dimension changes is desirable, expecially in view of the fact that magnetite does not obey

the laws of cubic symmetry in its magnetic behavior. With the apparatus here used there was not sufficient ease or accuracy of adjustment. Furthermore the locating of these axes in the sphere was difficult, their directions having been lost during the grinding process. The specimen did not appear to have cubic symmetry as regards magnetostriction, however.

The magnetic properties of crystalline iron have been studied by Beck and a summary of his work is given by Kunz.[8] The symmetry required by the cubical system is apparently not rigorously satisfied by the magnetic properties of iron crystals but the deviations are much smaller than in the case of magnetite. The writer has been unable

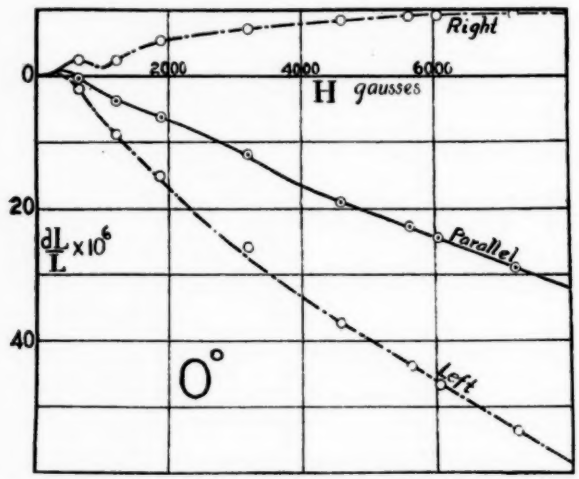

Fig. 5. Iron disk; plane parallel to H, and slightly to the right and to the left, as marked

to secure iron crystals large enough to make a sphere of the proper size for investigating magnetostriction. However, some plates of silicon iron alloy (about 3½ per cent Si) were available, in which the grains were of large size.

A single grain was cut from one of these plates and turned into a flat disk 1.7 cm in diameter and 0.07 cm thick. The magnetostriction apparatus for the longitudinal effect was then fixed to the edges of this plate and the disk supported vertically between the flat ends of two brass screws which pressed from opposite sides against the center of the disk. To make the mounting secure it was necessary to wedge the edges of the disk tightly into the slots in the heads of brass screws. These screw heads were then fitted tightly into holes on the magnetostriction ap-

[8] **Kunz,** Bull. Nat. Res. Council, **3,** 165, 1922

paratus. Rubber bands wound around the outside of the attached uprights increased the rigidity of connection.

In Figs. 5, 6, 7, and 8 are shown the results obtained with this iron disk in a longitudinal field. The relative change of length of a diameter of the disk is here plotted against the field strength H (measured in the absence of the disk) instead of against the magnetic induction. In connection with these curves it is to be remembered that the plane of the disk is vertical and at the same time parallel with the magnetic field. It very soon became apparent that slight errors in adjusting this plane parallel to H resulted in decidedly large modifications of the magnetostriction curves. For this reason three curves were obtained for each diameter of the disk which was investigated. The first curve was secured when the plane was to all appearances parallel with H. Two other

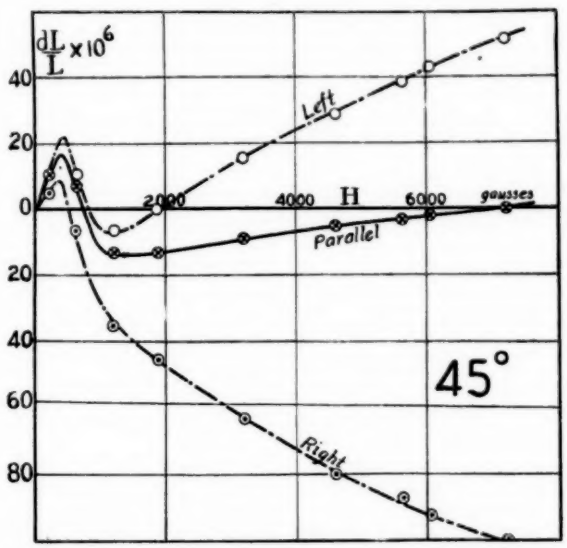

Fig. 6. Same as Fig. 5 but along a diameter at angle of 45° to the first

curves were then secured when the plane was turned successively through a small angle to the right and to the left of the parallel position. The three curves of Fig. 5 marked 0° were the first obtained in this way, the positions of the disk being indicated for each curve. The disk was then removed and replaced so that magnetostriction along a diameter 45° from the first could be observed. This set of three curves (Fig. 6) is marked 45°. In the same way the magnetostriction along diameters 90° and 135° from the first was measured and results plotted in Figs. 7 and 8.

The magnitude of the dimension changes is larger than has been previously found and in most cases the curves are not like those for ordinary iron. Hysteresis effects are not shown in the diagram, all the curves having been obtained with an increasing field. For some positions hysteresis was quite important; in one case the diameter of the disk expanded quickly to a certain point as soon as the field was produced and then continued to expand slowly for some time in this constant field. The intensity of magnetization of iron has been found to exhibit a similar viscous yielding.[9]

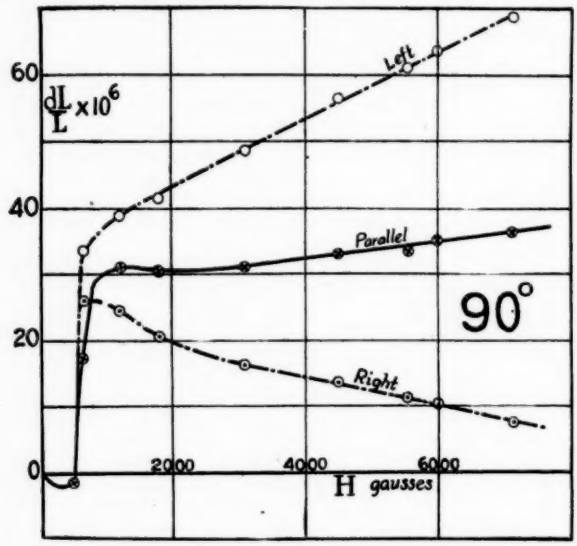

Fig. 7. Same as Fig. 5 but along a diameter perpendicular to the first

A possible source of error must be considered in connection with these curves. If the disk is not accurately parallel with the magnetic field a torque will be set up tending to twist the plane into line with the field. This torque will be opposed by the two screws between which the plate is clamped and the result will be a distortion of the disk which is not a true magnetostrictive effect. It appears from the curves that this error is not very large, for when the disk is turned to the right of the parallel position one would expect the error due to this torque to be in the same direction as when the plate is turned to the left of the parallel position. Except for very small fields the curves show that such is not the case. We may conclude, therefore, that these curves give a fairly accurate representation of the true magnetostriction effect, at least for large enough values of the field.

[9] Ewing, "Magnetic Induction in Iron," p. 127. A. M. Mayer (Phil. Mag. **46**, 177, 1873) has measured the time required for magnetic expansion to take place.

Making this assumption we may draw the following conclusions. The character of the longitudinal magnetostrictive effect may be completely changed by changing the direction of the magnetic field with respect to the crystal axes of the specimen; a contraction may be converted into an expansion. The complicated nature of these curves suggests that the field was never parallel to a principal axis of the crystal. The large effect produced by turning the plane of the disk slightly out of the direction of the field, especially for the 135° position, and the nature of the curves secured in this displaced position might indicate that a principal axis of the crystal does not lie in the plane of the disk. Such a conclusion might be reached by assuming that simple types of

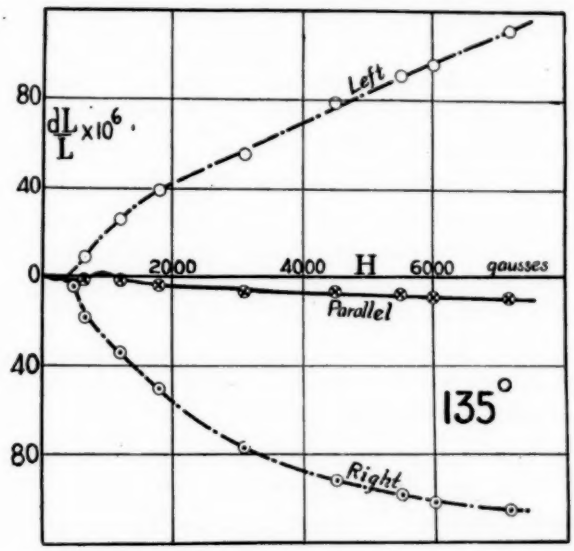

Fig. 8. Same as Fig. 5 but along a diameter at angle of 135° to the first

curves are obtained along the axes and more complicated combinations for other directions. It is possible, of course, that the grain does not possess a perfect crystalline structure, in which case little can be conjectured regarding the location of axes. A second grain, turned into a disk 1.48 cm in diameter, gave results similar to those described.

Discussion of Results with Reference to Theories

These investigations show conclusively the importance of crystal structure in relation to magnetostriction. The type of curve usually obtained with rings and bars is like the dotted curve marked "right" on the 45° diagram of Fig. 6, and attempts have been made to explain this curve on the basis of certain assumptions regarding molecular

structure. It now appears that a number of curves of different types will have to be explained. Before a correct model of the magnetic atom in iron can be constructed it will be necessary to investigate carefully the magnetostriction curves in relation to the axes of the iron crystal, for it appears that the effect is determined very largely by the direction of the magnetic field with respect to these axes.

Perhaps the most satisfactory type of model is the one recently proposed by Sir J. A. Ewing.[10] This model of the magnetic molecule consists of an outer fixed shell of magnetic elements and an inner movable magnetic mechanism resembling the original Weber element. The forces between the fixed outer shell and the inner element are supposed to determine the degree of stability of this inner element, and according to Ewing these forces may be capable of producing a distortion of the molecule. It is the outer shell which determines the ordinary mechanical or crystalline properties of the solid. A distortion of the outer shell could thus easily alter the forces exerted on neighboring molecules and thus produce dimension changes of the crystal.

Ewing supposes as an example that the outer shell consists of magnets at the corners of a cube, the axes lying along the diagonals of the cube and similar poles pointing inwards. The Weber element has eight magnetic poles at the corners of a cube and is capable of turning as a rigid system about the center. Four of the poles have one polarity and the four opposite poles have the other polarity. If an external magnetic field acts on this system it will tend to cause one of the magnetic axes of the Weber element to line up parallel with the field. If the one pole pertaining to this particular axis attracts the nearest poles of the outer shell more strongly than the other pole repels the poles of the outer shell which are nearest it we would expect a contraction of the molecule in the direction of the magnetic field. Contraction of the whole solid in this direction might then be produced. If on the other hand, the repulsion effect of the Weber element predominates the molecular diameter parallel to the field would elongate and the solid would expand in the direction of the magnetic field. Expansions or contractions transverse to the magnetic field would be produced, depending upon whether the repulsions or attractions of the remaining pairs of poles of the Weber element for the external shell predominated. If we suppose the poles of the external shell are not all of the same strength, or if they are not all similarly situated with respect to the inner element, which need not be pivoted at its center, it is easy to see that either contraction or extension of the molecule (and thus of the entire solid) could be pro-

[10] Ewing, Phil. Mag. **43**, 493, 1922

duced in different directions with respect to the magnetic field; also the direction of the field with respect to the molecule would be a factor in determining the nature of the dimension change.

It appears, therefore, that the latest model of Ewing's for explaining magnetic induction is adequate with scarcely any modifications for explaining the various magnetostrictive effects in crystals. It is hard to see how a simpler model could take account of the diversity of these effects.[11]

The experiments described above emphasize the importance of structure in relation to magnetostriction, so that one is inclined to consider Maxwell's stresses as playing a comparatively small part in the phenomenon. Theories based entirely upon these stresses have never been satisfactory. Another type of theory[12] has pointed out the reciprocal relations between strain and magnetization, e. g., if the length of an iron bar increases when it is in a magnetic field then a stretching of the same bar will increase its magnetization. This theory applied to the present experiments on iron predicts the possibility of diverse variations in magnetization depending on the direction of the strain with respect to the crystalline axes. Ordinarily iron has been found to show an increase of magnetization when stretched in a weak field and a decrease when stretched in a strong field, the critical field where no change is produced being known as the Villari reversal point. It now appears that this particular kind of Villari reversal is not necessarily characteristic of iron. It is probably a consequence of a certain heterogeneous arrangement of crystals in the iron specimens, and the separate crystals may or may not show this reversal.

A further study of the magnetostriction of different crystals is contemplated, in order to determine more accurately the relation of the effect to the crystal axes.

The writer is indebted to the research laboratory of the General Electric Company for very kindly supplying a number of pieces of silicon-iron alloy with large grains from which the iron disks described above were made.

THE RICE INSTITUTE,
HOUSTON, TEXAS
May 2, 1923

[11] Since this was written an article by Alpheus W. Smith has appeared (Phys. Rev. **22,** 58, 1923) in which the Ewing model is shown to account for magnetostriction, magnetoresistance, and change of thermoelectromotive force on magnetization — also the effect of strain on these phenomena.

[12] J. J. Thomson, "Applications of Dynamics to Physics and Chemistry," p. 47.

A VARIABLE SINGLE BAND ACOUSTIC WAVE FILTER

By G. W. Stewart

Abstract

Single band acoustic filter; simple method of varying the width of the transmitted band.—An extension of the earlier theory indicates that if the size of the orifice leading into the side tube is altered, the upper limiting frequency should change while the lower limiting frequency remains constant, thus changing the width of the band. The orifice is readily changed by introducing a cylinder of paper with punched holes of the proper size and position. Experimental results confirm the prediction as to the lower limit and give for three different orifices upper limiting frequencies of 455, 390 and 340 per sec., in fair agreement with the corresponding theoretical values 510, 440 and 385, respectively.

THE acoustic wave filter to be described is presented to illustrate the possibility of varying the width of the transmission band with but a slight alteration in the filter itself. It is not to be regarded as highly developed in form, for as yet little effort in that direction has been made.

Theory

For the sake of brevity reference will be made to a former paper[1] on the general theory, for equations and for the meaning of *impedance*, *inertance* and *capacitance*. The filter and its transmission curve are shown in Fig. 1 which is the same as Fig. 8 of that paper. The filter is drawn to scale, the length over all being 10 cm. In the previous article it was found that formula K gave the best agreement with experimental values. We will therefore make the assumptions involved in K', viz., that the orifice into the surrounding chamber has the inertance M_2', the conduit between two adjacent branches the inertance M_1, the chamber the capacitance C_2 and the branch tube leading to the outside, the inertance M_2. In addition, however, we will use a variable orifice at the opening from the conduit to the side tube and note the resulting change made in the transmission curve. The inertance of this orifice will be designated by M_2''.

According to Eq. (27)[1] the impedance of the side branch with the orifice represented by M_2'' omitted, is

$$(Z_2)_A = i\frac{M_2\omega(M_2C_2\omega^2-1)}{M_2C_2\omega^2+M_2'C_2\omega^2-1} \qquad (1)$$

[1] Stewart, Phys. Rev. **20**, 528, 1922

If we now introduce the orifice M_2'' in series, we have, since its impedance is $i\omega M_2''$,

$$(Z_2)_B = i\,M_2''\,\omega + i\frac{M_2\omega(M_2'C_2\omega^2-1)}{M_2C_2\omega^2+M_2'C_2\omega^2-1}$$

$$= i\frac{M_2''\omega(M_2C_2\omega^2+M_2'C_2\omega^2-1)+M_2\omega(M_2'C_2\omega^2-1)}{M_2C_2\,\omega^2+M_2'C_2\omega^2-1} \tag{2}$$

If the conduit has an inertance between the branch openings of M_1, its impedance Z_1 is $iM_1\,\omega$. The limiting frequencies of no attenuation can

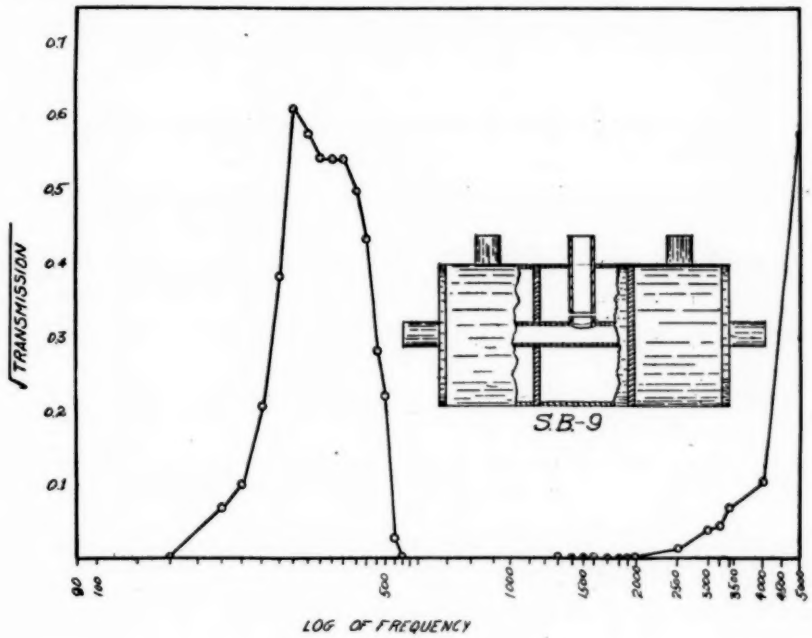

Fig. 1

now be ascertained by using $Z_1/Z_2=0$ and $Z_1/Z_2=-4$. If this is done, we find for the frequency $\omega/2\pi$ the following values:

$$f_1=\frac{1}{2\pi}\sqrt{\frac{1}{C_2(M_2+M_2')}} \tag{3}$$

and

$$f_2=\frac{1}{2\pi}\sqrt{\frac{M_1+4\,(M_2+M_2'')}{C_2[4M_2(M_2'+M_2'')+M_2'(M_1+4M_2'')\,M_1M_2]}} \tag{4}$$

Eqs. (3) and (4) show the interesting fact that the lower limiting frequency f_1 is independent of M_2'', whereas the upper limiting frequency f_2 is dependent upon M_2''. Thus, if the theory be substantially correct, the width of the band may be changed by altering the size of the orifice

represented by M_2''. In applying (3) and (4) the following measurements of the filter are substituted:

$M_1=\rho l_1/S_1$, $M_2=\rho l_2/S_2$, $M_2'=\rho/c'$, $M_2''=\rho/c''$ and $C_2=V_2/\rho a^2$.

In these, l and S refer to the length and area respectively, the subscripts having the same significance as already adopted; ρ is the density of the fluid, a is the velocity of sound, c' is the conductivity of the orifice into the volume M_2 computed approximately as an elliptical channel, and c'' is the conductivity of the circular orifice into M_2, numerically equal to twice the radius. The value of M_2' was $\rho/.455$.

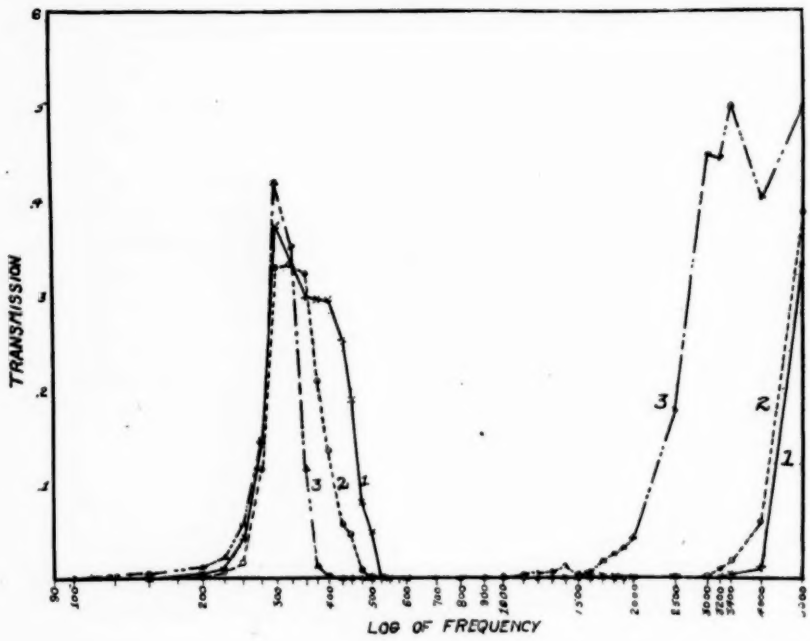

Fig. 2

Experiment

In order to introduce and to modify the orifice, a tightly fitting roll of heavy writing paper with holes of selected sizes was introduced into the conduit, the holes being centered in the branch tubes.

The transmission curves are shown in Fig. 2. Curve 1 is with the orifice 0.486 cm in diameter, the curve being the same as in Fig. 1. This orifice is really the end of the tube M_2, and is considered as part of it. Hence it does not give any value to M_2'' and $M_2''=0$. Curves 2 and 3 are for orifices with diameters of 0.3 cm and of 0.1 cm, respectively. As is clearly shown, the lower limiting frequency, taken as the

frequency for one-half of the maximum transmission, remains unchanged, as indicated by the theory. For the upper limiting frequency, we have the following experimental and corresponding theoretical values. The latter were obtained by Eq. (4) and are placed in parentheses. Curve 1, 455 (510); curve 2, 390 (440); and curve 3, 350 (385).

Discussion

The agreement between experiment and theory is satisfactory since it covers both points, viz., the constancy of the lower limiting frequency and the decrease of the upper limiting frequency with decrease in the size of the orifice.

The fact that the transmission increases appreciably at 3,200 per sec. in curve 1, and at lower frequencies in curves 2 and 3, is not anticipated in the present theory, which gives attenuation for all frequencies higher than those of the band. The extension of the theory which explains this increase of transmission has been made and will be presented in a later paper. As will be shown in later contributions, there are at least two ways in which this transmission at higher frequencies may be practically eliminated.

Physical Laboratory,
University of Iowa
March 17 1923

TINNITUS AND ITS RELATION TO NERVE DEAFNESS WITH AN APPLICATION TO THE MASKING EFFECT OF PURE TONES[1]

By John P. Minton

Abstract

Sensitivity curves for ears afflicted with tinnitus.—Patients suffering from tinnitus, or ringing in the ear, show a marked decrease in sensitivity for the range of frequencies of the subjective tones, and for this range there is a decided masking effect.

Masking effect for pure tones.—Tinnitus is associated with nerve lesions. These results, therefore, and also simple experiments with tuning forks, indicate that the conclusions of Wegel and Lane on the masking of objective tones may not be correct, and that the disturbance is in the nerve system and not in the mechanical system of the inner ear.

TINNITUS is the medical term used to identify the auditory disturbance which results in the production of tones and noises of a purely subjective origin. We shall omit the noises from consideration and focus our attention on the tones alone. These subjective tones seem to be just as pure and distinct as objective tones, such as are produced by tuning forks. They are sometimes of an intermittent nature and continue for a few seconds only at a constantly decreasing intensity. In extreme cases they become annoying and apparently continue indefinitely. Sometimes the intensity is constant and sometimes variable. Likewise, the frequency of tinnitus may be constant or variable or there may be a number of frequencies present. It has been pointed out that the phenomenon we are to consider is associated with nerve deafness. Most likely, the disturbance originates in the nerve system (including its endings) rather than in the mechanical system of the inner ear for in that case the mechanical parts would be vibrating at the various frequencies and this seems improbable in the absence of external forces.

Audibility curves have been obtained by the writer for patients having tinnitus associated with nerve deafness. These curves, together with the observations made at the time of the tests, show the relation between tinnitus and nerve deafness. The masking effect of the tones produced as a result of tinnitus on the objective tones supplied by a telephone

[1] The experimental work given in this paper was done while the writer was a National Research Fellow at Ryerson Physical Laboratory, University of Chicago.

receiver will be discussed together with the bearing of these results on the conclusions of Wegel and Lane in their recent paper.[2]

Experimental Results

The data for the curves shown below were taken by an audion oscillator and telephone receiver as described in an earlier paper.[3] The curves show the receiver current required for minimum audibility at the various frequencies compared with normal which was taken as 1.* All the curves

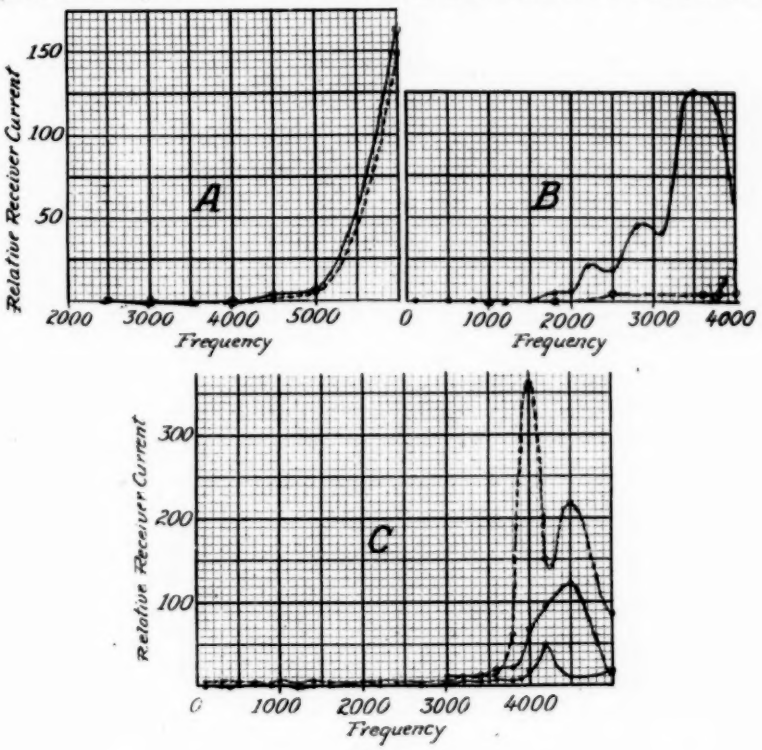

Fig. 1

are unique in that the depressions in audibility below normal occur over limited frequency regions within which all the pitches of the tinnitus tones are confined. Furthermore, the interference or masking effects occur only over these same regions.

Many audibility curves have been taken for cases of nerve lesions, but perhaps the few given below will be sufficient to illustrate the nature

[2] Wegel and Lane, Phys. Rev. **21**, 701, 1923

[3] Minton, Phys. Rev. **19**, 80, 1922

* In Figs. 1 and 2 the ordinate for the bottom line should be 1. Ratios less than 1 are shown below this line, distances proportional to their reciprocal, e. g. 1/10 being 10 divisions below.

of the results and to show the experimental basis upon which the conclusions rest. The right and left ears are represented by the circles and dots respectively. The figures are for four different individuals none of whom were conscious of any deafness, but all of whom complained of tinnitus. Each of the cases cited shows normal hearing up to a definite frequency. Above this frequency the hearing was depressed below normal and all the patients recognized the coincidence in pitch of the objective tones and the troublesome tinnitus tones. Difficulty was encountered over the depressed region in making a decision as to what intensity of the objective tones corresponded to the threshold value because of the presence of the subjective tones which interfered and partially masked the former sounds. Inasmuch as all the curves are normal below the depressed region it is quite certain that no masking effect was present here. The interference occurred, then, over a limited region in conformity with Wegel's and Lane's results with objective tones only.

The curves in Fig. 1B show that the left ear is normal except perhaps at the higher frequencies. The slight depression may be caused by the presence of tinnitus in the right ear which has the nerve lesion.

The curves for Fig. 1C were taken at different intervals extending over a period of five months, with a patient whose left ear had a serious case of tinnitus caused by an explosion. No trouble was present in the opposite ear.

Both ears of the patient whose curves are shown in Fig. 1A were affected by tinnitus which began at a frequency of 5000 per second in both ears and which coincides with the region of partial deafness.

Both ears were affected for the case shown in Fig. 2, the curves being taken at intervals covering a period of 2½ years. Tinnitus began at 2600 and ceased at 4500. It appeared to be centered around 4000 where the maximum depression in hearing occurred.

In passing it is worth while to observe that both ears of a patient are often affected alike both in degree and in frequency range. It is also important to record that the groups of nerves which have the auditory nerve lesions are the very same groups in which the tinnitus is set up. This appears to locate definitely the source of the tinnitus in the affected regions of the nerves themselves.

These observations have a direct bearing on the work of Wegel and Lane who concluded that the masking effect is of a dynamical nature and is brought about by vibratory motions of the basilar membrane. It seems, however, that the work of the writer in cooperation with the otologists shows that the same kind of interference is encountered in many abnormal cases of the nature cited in the present paper where

it is reasonably certain that the disturbing tones (tinnitus) originate in the nerves. Masking effects occur, then, for both objective and subjective tones, but at the present stage of the knowledge of the physiological processes involved in audition, it might be best to avoid speculation regarding the causes.

In conclusion attention may be directed to the marked masking effect observed when tuning forks are applied to opposite ears with no possible chance of conduction of sound from either fork to the ear on the opposite side of the head. Let two forks of the same pitch be set into vibration and one of them be held before one ear and a moment later the other one be placed near the opposite ear. If the second fork is vibrating with a little greater intensity than the first one, the tone in the first ear is masked by that in the second one and appears to shift

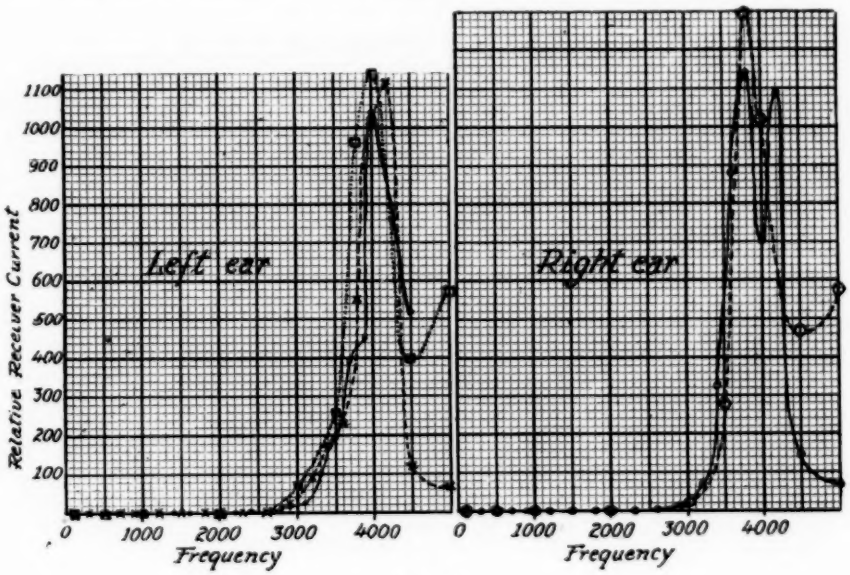

Fig. 2

from the first to the second ear. Even when the intensity of each fork is far too small (low pitch forks being used) to be heard by the opposite ear, the masking effect of the second fork may be complete. This test can easily be performed by anyone and is surely a convincing proof that the masking effect described is not necessarily a function of the cochlea of the same ear, as suggested by Wegel and Lane, but may more probably be a property of the auditory nerves or even of the acoustic centers of the brain itself.

RESEARCH DEPARTMENT, RADIO CORPORATION OF AMERICA,
NEW YORK CITY, May 7, 1923

A NEW METHOD FOR MEASURING THE TENSILE STRENGTH OF GLASS

By J. T. Littleton, Jr.

Abstract

Tensile strength of glass.—Lack of uniformity and reliability in the results hitherto obtained is due to the fact that the strength of the surface is greatly reduced by slight scratches. *The new method of measurement* here described attempts to eliminate as far as possible the effect of surface defects. A bar of glass is used which has been cut from the middle of a slab which had been heat treated in such a way as to leave the upper and lower surfaces of the bar under high compression, while the inside is under tension. When this bar is broken by bending, the tension introduced in the lower surface is largely neutralized by the initial compression, so that the maximum tension is not in the lower surface but in a zone nearer the neutral axis. The initial stresses are measured by means of polarized sodium light and a calibrated Babinet compensator, and these combined graphically with the stress due to the central load required to break the bar, give the maximum tension introduced which is taken as the lower limit to the strength of the glass. In this way values of 12 and 15 kg/mm^2 were obtained for a lead glass and a borosilicate glass, values twice as great as those given by the usual methods; and the mean deviation of individual measurements is less than half as great.

Introduction

THE tensile strength of glass has been studied extensively in the past by many different experimenters but with one exception,[1] the variations in results on any given glass have been so great that no conclusions could be drawn other than as to the general order of magnitude, and little as to the comparative values of different glasses could be definitely determined.

Winkleman and Schott[2] investigated the effect of composition on strength, studying a wide range of glasses. Their measurements were made on polished specimens. The absolute values obtained varied from 3.53 kg/mm^2 to 8.35 kg/mm^2. The variation in results on the same glass, being about 25 per cent, was so great that they selected the highest value as probably being the more nearly correct. Results obtained by later investigators are of the same order of magnitude. Winkleman and Schott further proved that glass was from ten to twenty times as strong under compression as under tension.

The measurements given by Kowalski[1] show a remarkable uniformity which is difficult to understand since his experimental procedure was

[1] Kowalski, Ann. der Phys. **36,** 307, 1887

[2] Winkleman and Schott, Ann. der Phys. und Chem. **51,** 697, 1893

not essentially different from that of others and since his results are of the same order of magnitude.

In more recent work, Griffith[3] used cracked bulbs subjected to an internal pressure up to the limit. The stresses around the cracks were computed according to the method developed by Inglis[4] and extended to apply to the conditions of his experiment. These results were checked by experiments on fine filaments. The values obtained are very high, being as great as 300 kg/mm^2.

The most obvious conclusion to be drawn from the work of these investigators is that all experiments made to date, with the exception of that of Griffith, have served to measure only the surface condition of the glass. Common experience shows how great are the effects of surface conditions, small file and diamond cuts making the specimen very easy to break. It has been demonstrated by Inglis[4] that stresses are increased around an elliptical discontinuity by twice the eccentricity of the ellipse and this explains why surface defects so greatly affect the strength of glass.

Theory of Present Method

The method used in this work has the advantage that while the specimen is being tested the maximum tension produced in the surface is much less than the tension produced inside, so that the effect of surface irregularities is less important. This result is accomplished by giving the specimens a preliminary heat treatment, a sudden chilling from the plastic state, which produces the desired initial distribution of stress, high compression in the surface and tension in the middle section. Let $-T_s$ and $+T_m$ represent the corresponding extreme values. If now a uniform tension is added by means of a straight pull, the algebraic difference between the maximum tension in the middle and in the surface will always be equal to the initial difference (T_m+T_s), and the fracture will be more likely to start inside the glass than if the specimen had been annealed. If the added tension at failure is L, then we know that either the surface broke at $L-T_s$ or the glass broke inside at a tension of T_m+L, and that the intrinsic strength of the glass is at least T_m+L.

A glass plate cooling rapidly from the plastic state has its surface set while the interior is soft. This gives after cooling a relative contraction of the interior causing the distribution of stress mentioned above.

[3] Griffith, Phil. Trans. Royal Soc. A 221, p. 163, 1920

[4] C. E. Inglis, Stress in a Plate Due to Cracks and Sharp Corners, Proc. Inst. Naval Arch. Mar. 14, 1913.

the surface under compression and a portion of the interior under tension. This state of strain can be represented by a curve such as No. 1 of Fig. 1. In these experiments the specimens used were rectangular bars, supported at their ends on two knife edges, and these were broken by loading at the center instead of by a straight pull. Such a load gives a tension on the under or convex surface changing uniformly to zero at the center and to a compression in the upper concave surface. When the breaking load has been measured and the maximum stress due to this load has been computed, the stress curve may be drawn as a straight line such as curve No. 2, plotted on the same scale of coordinates as No. 1. Then a combination of curves No. 1 and No. 2 give No. 3 which is the resultant curve of the stress in the glass at the instant of fracture. The

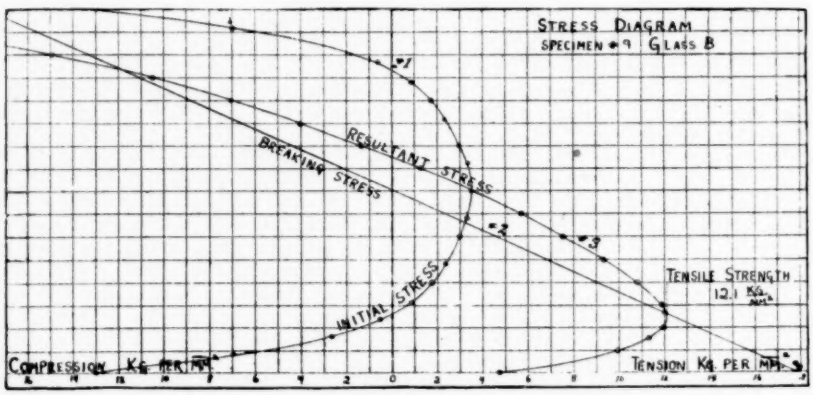

Fig. 1

maximum tension is immediately obtained and is seen to be at some interior point. It is further evident from this curve that the compression in the upper surface is quite high, but since glass is so much stronger under compression than under tension danger of fracture from compression is considered negligible.

The experiment then consists in measuring the original strain distribution in a sample of glass, then loading this sample until fracture occurs, and combining graphically the original stresses with the load stresses and noting the value of the maximum tension as the lower limit of the tensile strength of the glass.

Experimental Method

An optical method was used for the determination of the original stress in the sample to be broken, the apparatus being shown in Fig. 2. The strain pattern was photographed for convenience of measurement. The

amount of strain is proportional to the displacement of the usual Babinet line caused by the introduction of the strained sample.

Before this optical strain pattern can be transferred to a stress diagram, it is first necessary to calibrate the apparatus and determine the birefringence constant of the glass studied. This was accomplished by placing known loads on an annealed rectangular bar on the glass and measuring the optical strains produced in terms of the displacement from the initial position of the Babinet line. Fig. 4 shows the strain produced by loading at the center a rectangular bar supported at its

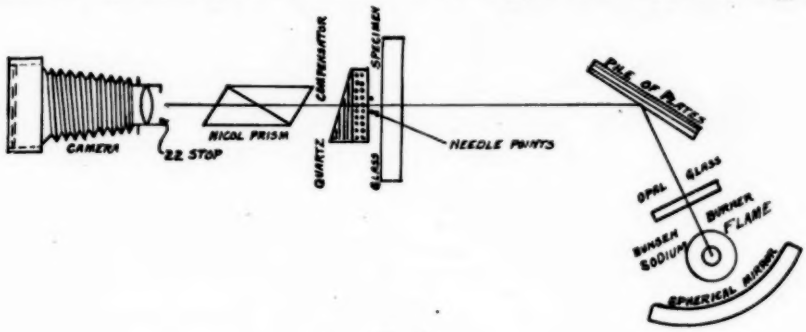

Fig. 2

ends. The stress in the under surface of the glass was then computed by means of the formula $S=3LW/2BD^2$ where S = stress, L = distance between knife edges, W = applied load, B = width of glass, D = thickness of glass in direction of load, the units being kilograms and millimeters. By adding different loads and measuring the displacements, a linear relation between stress and displacement was observed.

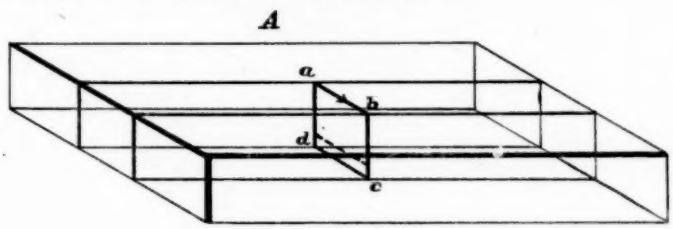

Fig. 3

Such an optical system measures only integrated effects of the strain at right angles to the light path. That is, if the light ray passed through a region of compression and also one of tension then only the resultant of the two is subject to measurement. But it is the intensity of the stress at a point which counts and not the average over an area. In the case of a suddenly cooled rod of circular or square cross section, cooling will take place in such a manner that the stress along any straight line

perpendicular to the length varies from point to point. But if the bar have a width large with respect to the thickness there will be a section in the center where the isothermal lines during cooling will be practically parallel to the surface and if this section be cut out of the slab after cooling, the strain along such a line will be constant.

In the case of a slab of glass suddenly cooled and thereby highly strained, such as *A*, Fig. 3, it is evident that the strain perpendicular to the plane *abcd* in the center of the slab will vary from point to point

Fig. 4

Fig. 5

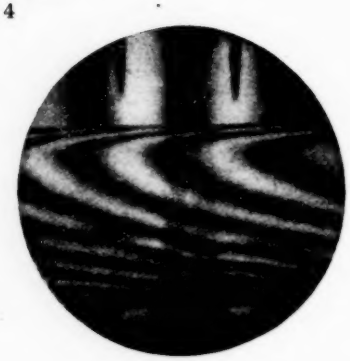

Fig. 6

Fig. 4. Stresses in annealed glass bar due to bending
Fig. 5. Initial stresses in heat treated glass bar
Fig. 6. Bending stresses combined with initial stresses in heat treated glass bar

on *ad* as shown by curve No. 1 in Fig. 1 but will be constant along lines parallel to *ab*. If, therefore, the specimen be viewed along the line *ad* the compression and tension should balance and the resultant strain as measured by the Babinet compensator should be zero, but the strain measured looking along *ab*, after the central section has been cut out, gives very nearly the maximum strain in that plane and not simply the average, since the two are approximately equal.

All specimens tested were bars of approximately square cross section, 5 mm to a side, cut from slabs chilled in oil from a temperature above

the annealing point of the given glass. The top and bottom surfaces were untouched but two sides were carefully polished. The distance between knife edges was 10 cm. A photograph was obtained showing the strain pattern for the unloaded bar, such as shown in Fig. 5, using a sodium flame as a source of light. This was then quite simply converted to a stress diagram such as curve No. 1, Fig. 1, and was combined with the breaking stress, curve No. 2, giving the resultant stress curve No. 3, Fig. 1, and thus the maximum tension in the specimen. A photograph showing the strain pattern for a loaded bar is reproduced in Fig. 6.

The breaking stress was measured by loading gradually with shot at the center of the bar. The two end knife edges were mounted on rollers so that the possibility of a torque being applied was minimized.

Measurements are given for two glasses of widely different composition, glass A being a borosilicate and glass B being a lead glass.

TABLE I

T S = Tensile strength in kg/mm²
C = Initial compression at the edge in kg/mm²
Var. = Mean percentage variation from the mean

Glass A

Annealed		*Strain 1*			*Strain 2*		
No.	T S	No.	C	T S	No.	C	T S
1	10.73	1	2.15	8.70	1	8.61	14.20
2	5.86	2	2.86	7.20	2	10.30	16.60
3	7.06	3	2.87	7.50	3	8.80	14.40
4	7.70	4	2.94	12.00	4	11.77	14.46
5	5.66	5	2.74	10.70	5	9.73	14.32
6	7.21	6	3.50	12.06	6	8.48	12.12
7	6.24	7	3.33	10.32	7	10.60	14.04
8	7.31	8	2.64	9.14	8	10.70	16.69
9	6.42	9	3.44	10.40	9	10.02	15.51
10	7.82	10	3.45	7.08	10	8.69	14.68
Mean	7.20	Mean	2.99	9.52	Mean	9.96	14.74
Variation	13.3%	Variation		17.74%	Variation		6.20%

Glass B

Annealed		*Strain 1*			*Strain 2*			*Strain 3*		
No.	T S	No.	C	T S	No.	C	T S	No.	C	T S
1	6.80	1	3.96	9.02	1	8.04	10.54	1	11.99	13.56
2	7.59	2	4.80	7.64	2	8.68	13.28	2	11.20	13.40
3	8.30	3	6.14	8.68	3	9.59	10.03	3	10.11	12.40
4	5.70	4	3.90	8.50	4	9.01	12.17	4	10.99	12.30
5	5.48	5	3.80	6.00	5	8.38	10.57	5	13.83	13.90
6	7.19	6	4.16	7.88	6	10.29	9.48	6	13.00	11.97
7	7.66	7	4.05	6.33	7	11.08	11.17	7	12.71	11.20
8	8.66	8	3.81	7.28	8	12.08	11.70	8	11.35	11.15
9	7.01	9	2.73	9.58	9	7.53	11.34	9	13.09	10.72
10	12.09	10			10	8.79	13.50	10	9.71	11.61
Mean	7.64	Mean	4.15	7.88	Mean	9.35	11.38	Mean	11.80	12.22
Var.	16.0%	Variation		12.0%	Variation		8.8%	Variation		7.3%

It is evident from these data that as the strain is increased the tensile strength as measured has increased and the uniformity of the results has increased. While it cannot be stated that in the higher strained specimens the surface effects have been entirely eliminated, for in all

cases when the maximum load was added there was tension in the surface, it is quite evident that by this method surface effects are decreased and hence the internal strength is more nearly measured than by any method which does not take them into consideration.

It should be pointed out that it is possible that fracture starts on the side surface instead of on the under surface as in the case of the annealed glass. Referring to the drawing Fig. 3, at some point in the lines *cb* or *ad*, compression is neutralized and tension exists, the distribution being as shown in curve No. 3, Fig. 1, for the loaded piece. The dotted line represents the line of maximum tension. The probability of a flaw existing in the immediate region where the line cuts the surface is not as great, however, as in the surface bordering along the line *cd*.

The tensile strength of the annealed specimens is about what would be expected from the results obtained by Winkelman and Schott, but the strength of the highly strained samples is practically twice that of the other measurements. This result is attributed entirely to the effect of the initial surface compression, tending to decrease the surface effects.

The question might be raised as to the effect on the structure of the glass caused by such a heat treatment. There is nothing available to suggest that such an effect is to be expected. There is no proof of any structure in the glass and if the glass be a perfectly homogeneous isotropic material when annealed, the heat treatment given in chilling would not cause any change. Furthermore it is to be noted in the curve of resultant stress that the maximum tension exists at a point practically free of any initial stress, that is very near to the neutral zone of stress, and if fracture took place at this point no effect of strain on the strength could have affected the value obtained.

No claim is made that these results represent the final value for the ultimate strength of glass. The indication is that the strength is higher than the values published here, for the higher the initial compression the higher the final value obtained. The method will be extended to circular rods if possible and thus eliminate entirely the surface effect.

The author desires to express his appreciation to the Corning Glass Works Laboratory force for their assistance and cooperation and particularly to Miss Evelyn H. Roberts who did a large part of the detail of the experimental work.

PHYSICAL LABORATORY,
CORNING GLASS WORKS, CORNING, N. Y.,
May 7, 1923.[5]

[5] Essentially this paper was presented before the American Physical Society, April 23, 1920. Abstract in Phys. Rev. **15**, 520, 1920.

NOTE ON TREVELYAN'S ROCKER

By S. Bhargava and R. N. Ghosh

Abstract

Trevelyan rocker; experimental test of the gravity theory.—According to this theory, the two edges are alternately pushed up by the expanding lead, and then pulled down again by gravity; if so the square of the period of vibration is approximately given by: $T^2=(32k^2/a)\beta$, where k is radius of gyration, $2a$ is distance apart of edges and β is the maximum angular amplitude. Frequencies computed by means of the expression, using values of β determined by photographing the trace of a beam reflected from a mirror mounted on the rocker, agree closely with the actually observed frequencies. The effect of adding a load on the handle is also in agreement with the theory. Though elastic vibrations are also sometimes present, giving a faint high pitched sound, no Chladni figures could be obtained, so the transverse vibrations are relatively weak.

IN A RECENT paper,[1] Chuckerbutty questions the validity of the theory that the musical sound of the rocker is due to its rocking movement. Quantitative results he obtained do not agree with conclusions drawn from the mechanical theory; hence he concludes that the sound is due to the elastic vibrations of the system. The present authors therefore undertook a fresh investigation to determine the nature of elastic vibrations, if any. This note describes experiments whose results, however, tend to show that the mechanical theory of rocking movement is correct.

Mechanical Theory

The rocker generally consists of a 10 cm long brass prism of triangular

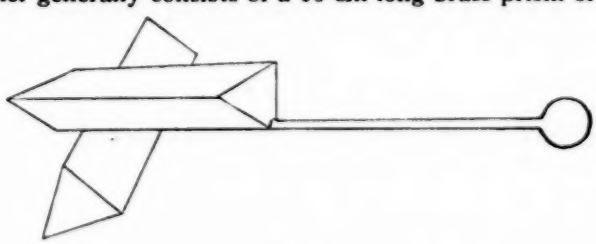

Fig. 1

section, at the lower edge of which there is a groove running parallel to the axis of the prism. To one end of the prism a 20 cm long thin rod fitted with a knob at the other extremity, is fixed, the whole forming a rigid system. When the rocker is heated strongly and placed so that two

[1] Chuckerbutty, Proc. Ind. Assn. for Cultivation of Sci. 6, 145 (1921)

ridges of the groove rest upon a cold clean lead block as shown in Fig. 1, a musical note is produced.[2] That the system rocks right and left can be easily observed, as described later, by attaching a concave mirror to the rocker and reflecting a spot of light which follows its motion. The general explanation of the maintenance is that the lead block expands at the line of contact with the ridges, and gives an impulse to the ridge which makes the better contact, pushing it up and thus tilting the rocker. A similar impulse is then given by expansion at the other ridge. In this manner the rocker is tilted right and left periodically on account of the expansion of the lead block, and the vibration continues until the lead block[3] becomes too hot. The impulses have no period of their own, but the period may be taken to be that of the free rocking motion of the system under the action of its own weight.

The mechanical or gravity theory of the free rocking motion can be simply obtained as follows. Let $A\ B\ C\ D$ and $A'\ B'\ C\ D'$ represent the equilibrium (horizontal) and the displaced positions, then we must have, neglecting damping,

$$-Mk^2\frac{d^2\theta}{dt^2}=Mg\cdot CP=Mg(a-h\ \sin\theta)\ \cos\theta \tag{1}$$

where Mk^2 is the moment of inertia of the system about either ridge, θ the angular tilt measured from the equilibrium position, $2a=CD$

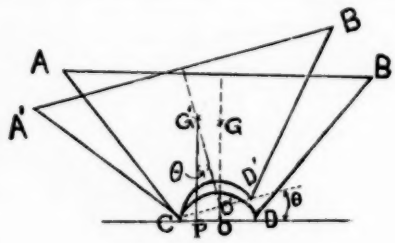

Fig. 2

distance between the two ridges, and $h=OG$ the distance of the centre of gravity from the plane containing the ridges. Since θ is small, Eq. (1) reduces to

$$\frac{d^2\theta}{dt^2}=\frac{hg}{k^2}\left(\theta-\frac{a}{h}\right) \tag{2}$$

Putting $x=\theta-a/h$, and μ^2-gh/k^2, we obtain

$$d^2x/dt^2=\mu^2x \tag{3}$$

[2] The rocker has generally to be started by a tap

[3] Lead is selected for its high expansibility and low conductivity

Let us suppose that we begin to count time when one of the ridges reaches its maximum upward position, so that at $t=0$, $\theta=\beta$, and $d\theta/dt=0$. The ridge comes down and reaches its equilibrium position after a quarter period, hence at $t=T/4$, $\theta=0$.

After performing a simple integration we obtain

$$-\mu T/4=\log\,[1-(2\beta h/a)^{\frac{1}{2}}] \tag{4}$$

or

$$T/4=k(2\beta/ga)^{\frac{1}{2}} \text{ approx.} \tag{5}$$

Eq. (5) shows that the period of oscillation is proportional to the square root of the maximum angular tilt for a given size of the rocker. When β decreases, the period decreases too, hence a rise of pitch is generally observed as the motion dies. When β is nearly equal to zero, the frequency according to (5) should be infinite, but this is actually not the case, Eq. (5) does not in fact hold good beyond a certain minimum value of β. The physical limit of β depends upon the damping of the system, and as soon as this value is attained the motion subsides at once.

Eq. (5) can be tested experimentally when β is known for a rocker of given dimensions. To find β the vibration curve of the motion of the rocker is obtained, then β is calculated from the distance at which the photograph is taken. By changing the numerical value of k, Eq. (5) can be further tested.

Experimental Observations

In order to photograph the vibration curve, a small concave mirror of large focal length was fixed to the knob of the handle bar of the rocker. By throwing a fine spot of light from an arc lamp and reflecting it from the mirror upon a sliding photographic plate when the rocker is producing a musical note, the vibration curve was obtained, and in order to determine the frequency, the trace of a point on a vibration tuning fork of known frequency was simultaneously photographed. The frequency was at the same time determined by a sonometer. Table I gives the results of a few observations.

Table I

Dimensions of the rocker: $2a=7$ *cm;* $h=.95$; $k^2=2.6$

Amplitude of vibration curve	Distance from mirror	From curve	Frequency by sonometer	Calculated by Eq. (5)
1.07 cm	210 cm	265	265	254
.335	114	325	323	339
.51	178	328	327	338
2.10	86	166	615	614
.75	114	220	221	224
2.3	200	174	175	170

Table II taken from the paper of Chuckerbutty[1] gives the results of his observations and those calculated with the help of (5). From these tables it is clear that the observed and calculated values agree within experimental errors, and consequently the musical note is due to the rocking movement of the system.

In order to find out if the handle bar took part in producing a musical note by its transverse vibration, two rockers having different lengths of the handle bar were selected, one having a handle about a meter long, the other a short one, and the effect of placing a load of fixed size at different points of the handle bar was observed in each case when the rocker was oscillating and emitting a musical note of a definite pitch. By carefully placing the load, the angular amplitude of oscillation upon which the pitch depends, was kept almost the same. It was found that the lowering

TABLE II

Experiments of Chuckerbutty

k=4.8 (calculated empirically)[4]

Amplitude of vibration curve	Distance from mirror	Frequency	
		Observed by sonometer	Calculated by Eq. (5)
.70	98	121	126
.64	98	130	127
.60	98	136	135
.50	98	145	147
.20	98	180	210

of pitch was the same whatever the position of the load. In the case of transverse vibrations of the handle bar the lowering of pitch would certainly vary with the position of the load. On the other hand for the type of rocking motion contemplated, the lowering of the pitch should be the same, since the increase of moment of inertia is the same for all positions of the load on the handle bar, since it is parallel to the plane of the ridges. Hence it is concluded that there are no appreciable transverse vibrations of the handle bar. Furthermore, different loads of definite sizes (masses varying from 50 to 200 grams) were placed upon the knob of the handle bar when the rocker was oscillating. It was found that the ratio T/T' where T and T' are periods before and after loading, is definite for the same load, and does not depend upon the initial value of T. This at least shows that the vibrations producing the musical note are of simple character, and lends support to the theory of the rocking motion about either ridge.

[4] The empirically determined value of k differs from that of Chuckerbutty calculated by him from the dimensions of the rocker, due to the wooden block pressing the needle, since the inertia of the wooden block was neglected by him.

These experiments show that the musical note is due to the rocking motion. That certain elastic vibrations due to impact against the lead block are sometimes present, can be easily observed with the unaided ear, which recognizes the presence of the high pitches produced. In order to examine them more fully, Chladni's method of sand figures was employed. When the rocker was in motion, dry sand was thrown upon its flat face but the authors failed to obtain any sand figures. Hence the transverse vibrations of the body of the rocker, if present at all, are very feeble. Therefore the main part of the musical note whose intensity is so large, must be due to the rocking motion only.

ADDENDUM. In a very recent issue of Philosophical Magazine (May 1923) E. G. Richardson has described experiments conducted on different lines which confirm the gravity theory.

DEPARTMENT OF PHYSICS,
ALLAHABOD UNIVERSITY,
January 4, 1923.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE PASADENA MEETING, SEPT. 18, 1923

The 122nd meeting of the American Physical Society was held in the Norman Bridge Laboratory of Physics, California Institute of Technology, Pasadena, California, on Tuesday, September 18, 1923. The program extended over two sessions, the afternoon session being a joint session with the American Astronomical Society. The attendance was about 60. The presiding officer was Professor E. C. Watson.

Abstracts of the 18 papers presented by members of the Physical Society are given below. Numbers 1, 2, 3, 5 and 15 were presented at the joint session. The titles of the eight papers contributed by the Astronomical Society at the joint session are as follows:

19. **The absorption line O-type stars.** J. S. PLASKETT, Dominion Astrophysical Observatory.
20. **A possible origin of the nebular lines.** H. H. PLASKETT, Dominion Astrophysical Observatory.
21. **Regularities in the arc spectrum of zirconium.** C. C. KIESS AND HARRIET KNUDSEN KIESS, U. S. Bureau of Standards.
22. **The possibilities of instrumental development.** GEORGE E. HALE, Mount Wilson Observatory.
23. **On atmospheric absorption.** H. L. VANDERLINDEN, Observatoire Royal, Uccle, Belgium.
24. **The sun's action on the magnets. A note on variable stars and cosmic clouds.** LUIS RODES, Observatorio del Ebro, Spain.
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D. L. WEBSTER,
Secretary of the Pacific Coast Section.

ABSTRACTS OF PAPERS

1. The vacuum spark spectrum of calcium. J. A. ANDERSON, Mount Wilson Observatory.—A powerful spark was passed between metallic calcium electrodes 6 mm in diameter. The maximum instantaneous value of the current was about 10,000 amperes, and the electrode separation 2 mm. The sparks were passed at the rate of one in 5 seconds. Four hundred such sparks were sufficient for a full exposure with a one meter focus concave grating. The spectral range from λ 2000 to λ 6600 was covered, and the wave-lengths determined to a probable accuracy of ±0.03 A. After removing lines due to impurities and to residual gas as far as possible, there are left some 850 lines of which 46 are known calcium lines. The remaining 800 lines are presumably to be ascribed to ionized calcium, and their irregular distribution suggests that they belong to the doubly ionized atom. Many of these lines compare favorably in intensity with the strongest known calcium lines.

2. Series spectra in oxygen and sulphur. J. J. HOPFIELD, University of California. —Two of the oxygen series reported previously (Phys. Rev., **21**, 710, 1923) have been extended, $OP_{123}-mS$ to $m=7$, and $OP_{123}-mD$ to $m=7$. OP_1-1s is definitely absent. Using SO_2 the sulphur spectrum has been extended from λ 2500 to λ 350. SO_2 has an absorption band between λ 2500 and λ 1700 and another extends from λ1650 into the extreme ultra-violet. The many-line spark spectrum reaches to λ 350. The arc spectrum has a number of triplets of constant frequency differences. The designations of these by analogy with oxygen and their wave-lengths are: $OP_{123}-1S$, λλ 1823.35, 1820.53, 1807.42; $OP_{123}-2S$, λλ 1436.92, 1433.27, 1425.11; $OP_{123}-3S$, λλ 1326.69, 1323.58, 1316.63. $OP_{123}-2D$, λλ 1485.53, 1481.66, 1472.99; $OP_{123}-3D$, λλ 1412.92, 1409.41, 1401.55; $OP_{123}-4D$, λλ 1313.22, 1310.26,—(probably hidden). $OP_{123}-1s$, λλ 1914.96, 1900.47. OP_1-1s is absent. $1s$ has been obtained by Meissner (Ann. der Phys. **50**, 713, 1916). Hence OP_{123} has the values 82982, 83156 and 83554. Also $1S=28227$, $2S=13384$ etc. The new oxygen and sulphur spectra have a corresponding line missing and the triplets are inverted in intensities and separations as compared with the other spectra. OP_{123} is probably the valence level. Apparently there exist one stable and two metastable forms of the two elements with 9.11 and 13.56 volts, 6.50 and 10.31 volts the resonance and ionizing potentials of oxygen and sulphur respectively.

3. Extreme ultra-violet spectra. R. A. MILLIKAN and I. S. BOWEN, California Institute of Technology.—(1) The wave-lengths of about 1000 new ultra-violet lines of the elements of low atomic number are herewith reported. (2) The positions of the observed lines of the L spectrum of sodium and magnesium are shown to be accurately predicted by the Bohr theory. (3) Evidence is presented that the strongest lines of the extreme ultra-violet spectra of the elements from boron to chlorine correspond to atoms stripped of all their valency electrons.

4. Accurate measurements of the energy content of extreme ultra-violet mercury lines and the precise determination of the photoelectric long wave-length limit of a clean surface of mercury. C. B. KAZDA, California Institute of Technology.—In view of much discussion as to the effect of surface films on photo-currents and long wave-length limit, extraordinary precautions have been taken to obtain mercury surfaces completely free from all surface impurities. These are found to yield strong photo-currents for all wave-lengths as short or shorter than 2700 A but no photo-currents whatever for the line 2804 A of much greater intensity. These experiments fix definitely a long wave-length limit of a clean surface of mercury at about 2735 A. In these experiments the accurate measurement of the energy content of mercury lines has been carried down to 2253 A. This line gave a thermopile deflection accurately reproducible to six percent.

5. Panchromatic film characteristics in the ultra-violet. GEORGE R. HARRISON and CEDRIC E. HESTHAL, Stanford University.—Light from a cadmium spark was resolved with a quartz spectrograph, and exposures of various times and intensities were taken for thirteen wave-lengths from 2140 to 4850 A on Eastman panchromatic film. Elon-hydrochinon developer was used. Intensities were reduced by a set of calibrated screens of wire mesh. The resulting densities were plotted for each wave-length on a three-dimensional scale against $\log_{10}$ time and $\log_{10}$ intensity. It was found that the diminished contrast hitherto noted in the violet, which indicated very little contrast for the ultra-violet, was probably due to low intensity values, since high contrast was obtained in the present case even at 2144 with moderate intensities. Low contrast was obtained around 2350; hence the ultra-violet has just such maxima and minima as the visible. The decreasing sensitivity of the film, particularly noticeable below 2400 A, is due to greater inertia of the emulsion; i.e. the variation in speed with wave-length has more effect than the variation of contrast. Speed decreases noticeably below 2300 A. A study of the characteristic surfaces obtained indicates that the reciprocity law is quite as good an approximation in most cases as Schwarzschild's law. A detailed report will shortly be published elsewhere.

6. Magnetic beta ray analysis of soft x-rays. JOSEPH A. BECKER, California Institute of Technology.—Electrons of 300 to 1500 volts stimulate soft x-rays by impact on a target placed close to a radiator. The photo-electrons ejected from this radiator by these rays are made to produce a magnetic spectrum on Schumann plates after the method used by De Broglie in the analysis of hard x-rays. Most of the plates show a surprising concentration of the photo-electrons at the velocity corresponding to the x-ray frequency given by $Ve = h\nu = \frac{1}{2}mv^2$ where V is the initial applied potential. This indicates either (1) that there is a much more complete transformation in the case of soft rays than in that of hard, of the electronic energy into the equivalent radiant energy $h\nu$ and a second quite complete transformation of this radiant energy to kinetic electronic energy; or (2) that a much larger proportion of the initial incident electrons retain their initial velocity after two "reflections" than has hitherto been supposed.

7. The appearance of certain "ghosts" in the general radiation spectrum when x-rays are reflected from calcite crystals: An explanation of their cause and the means of their elimination. A. E. HENNINGS, Stanford University.—The appearance of "ghosts" in x-ray spectra has been noted in connection with previous work. (D. L. Webster and A. E. Hennings, Phys. Rev. **21**, 214, 1923.) When x-rays are reflected from the 010 face of a calcite crystal, "ghosts," due to reflections from the 011, 021, and $0\bar{2}1$ planes, are likely to appear. If one pair of edges of the 010 face are initially parallel to the incident beam a slight tilting of the crystal will cause the "ghosts" to shift, those due to the 011 and 021 planes moving one way and that due to the $0\bar{2}1$ planes moving in the reverse direction. These "ghosts" need not be encountered at all in the case of reflections below the second order from the 010 planes, since the exciting voltages for them are two or more times as large as that for the principal reflection. Should they appear in the higher orders they may be eliminated by properly tilting the crystal, which either causes the "ghost" to be thrown beyond the range of the vertical slit or decreases the angle of incidence for the particular set of planes to the extent that the exciting voltage for them exceeds the one employed.

8. The wave-length and intensity of scattered x-rays. P. A. Ross, Stanford University.—Spectrograms were shown of the molybdenum α_2 and α_1 lines scattered by paraffin, aluminium, copper, zinc, silver, and lead. The scattered radiation showed two diffuse lines whose breadth was about twice the distance between the α lines. One scattered line was unchanged in frequency while the other was shifted by an amount agreeing approximately with the theoretical equation

$$\Delta\lambda = (2h/mc)\sin^2\tfrac{1}{2}\theta = .0484\sin^2\tfrac{1}{2}\theta.$$

The shift for paraffin was measured at 30°, 60°, 75°, and 90°. The amount was independent of the nature of the scattering substance but the relative intensity of the shifted to the unshifted scattered line decreased with increasing atomic number. Since the wave-length of the scattered radiation increases with the angle of scattering, the amount of shift could be measured most accurately by means of a screen having an absorption limit slightly longer in wave-length than the unscattered radiation, by observing the angle at which a sudden increase of transmission took place. Curves relating absorption to angle of scattering were shown for molybdenum K radiation and yttrium absorption screen, tungsten with holmium screen, and platinum with lutecium screen. The curves indicate broad diffuse lines with centers of gravity shifting nearly according to theory.

9. The crystal structure of benzene. JARED KIRTLAND MORSE, University of Chicago.—In a paper before the American Chemical Society, September 1922, the author presented a molecular theory of the structure of the aromatic hydrocarbons which assigned a centered ortho-rhombic lattice to benzene and calculated the lattice constants. The values obtained were $a_1:b_1:c_1 = 5.664:7.090:6.172$ in A.U. using Richard's density and Groth's crystallographic measurements; and $a_1:b_1:c_1 = 5.697:6.996:6.137$ in A.U. from naphthalene. Since then Broomé obtained x-ray data from powdered benzene crystals but could not find a satisfactory lattice. This paper shows that plane spacings calculated by Hull's method for this centered ortho-rhombic lattice agree satisfactorily with Broomé's results for the lattice constants $a_1:b_1:c_1 = 5.809:6.884:6.186$ in A.U. The results are given in a table. The mean of the adjacent angles for two pairs of lines are 21° 21′.5 and 23° 39′.5 respectively. The scattering angles for *liquid* benzene for the $K\beta$ and $K\alpha$ radiation of iron are 21° 21′ and 23° 39′. Hence these regions are identified with the liquid. All other lines obtained experimentally are accounted for by this lattice within the limit of experimental error except three faint lines near the central image which may be due to the apparatus.

10. Effect of temperature and surface impurities on photo-currents with aluminium surfaces from which surface films have been removed by melting in vacuo. J. RUD NIELSEN, California Institute of Technology.—(1) Photo-currents are found accurately independent of temperature. (2) Photo-currents from Al remain strong after elimination of surface impurities, thus indicating that the disappearance of photo-currents by cleaning previously reported by other observers is due to pushing of the long wave-length limit beyond the range of wave-lengths used, rather than to a fundamental dependence of the photo-effect upon a surface film. (3) An apparent large change in photo-currents with temperature has been found due to the effect of temperature on the appearance or removal of surface impurities.

11. The pulling of electrons out of metals by intense electrical fields. ROBERT A. MILLIKAN and CARL F. EYRING, California Institute of Technology.—(1) Electron currents pulled from untreated tungsten surfaces by electrical fields, ("field-currents") begin at about 200,000 volts per centimeter and rise a billion fold, approximately reversibly, as the potential gradient is increased to 1,000,000 volts per centimeter. (2) The critical potential gradient may be increased four fold by heat treatment and two fold by producing large field-currents without heat treatment. (3) The rate of increase of field-currents with voltage is large when the critical potential gradient is small, and vice versa. (4) Large currents drawn from surfaces which have been subjected to intense heat treatment show a fatigue effect which recovers with the time. (5) The field-currents are completely independent of temperature between 300 K and 1000 K. (6) The field-currents are slightly greater at 1100 K than at 300 K presumably because of the increasing penetration of the field, with increasing strength, into the molecular or crystalline interstices of the surface. (7) The field-currents in

general have their origins in a very few minute surface spots which presumably locate surface impurities.

12. On the condition known as electrical neutrality. FERNANDO SANFORD, Stanford University.—It is well known that the electrical state of a body inside a closed hollow conductor and in electrical contact with its walls, is not at all influenced by the electrical condition of the enclosing conductor, and that the inside body always remains in electrical equilibrium with surrounding uninsulated bodies upon the earth. It necessarily follows that if the earth has an electrical charge, the enclosed conductor has a corresponding charge, and that if the electrical potential of the earth at the place of observation changes, the charge upon the enclosed conductor must also change. Experiment shows that there is a diurnal variation in electric potential between two conductors inside the same hollow conductor if one of them be kept insulated and the other be kept in contact with the enclosing conductor. Since the charge on the insulated conductor cannot change, this potential variation must be due to a diurnal variation in the potential of the earth at the place of experiment. It is concluded that neither the earth nor a body in contact with the inside of a closed hollow conductor is in the condition known as absolute electrical neutrality, and that such a condition is not known to exist on the earth.

13. Oscillograms of the Barkhausen effect. S. R. WILLIAMS, California Institute of Technology.—By means of a three step amplifier Barkhausen was able to detect certain electromagnetic effects in iron when magnetized. The minute e.m.fs. thus developed give rise to a rustling sound in the telephone receiver attached to the output side of the amplifier. Using an oscillograph, these small currents have been studied and analyzed. It is clear that a part of each curve is due to the free period of the telephone diaphragm. An attempt is now being made to find the real electromagnetic effect in the iron when magnetized, by replacing the telephone receiver with a string galvanometer.

14. Magnetic results obtained on the Carnegie during cruises IV, V, and VI, 1915–1921. J. P. AULT, Carnegie Institution of Washington.—The final results of magnetic observations made on the *Carnegie* during 1915–1921, have now been reduced and are ready for publication as one of the series bearing the general title "Researches of the Department of Terrestrial Magnetism." A discussion of the magnetic chart differences shows a steady improvement in the ocean magnetic charts since the beginning of the Department's ocean survey. A special report by W. J. Peters on the final magnetic results obtained on board the power schooner *George B. Cluett* during a cruise along the Labrador coast and into Hudson Bay and return in the summer of 1914, will be included also. A preliminary discussion of the magnetic secular variation over the ocean areas as based upon all the ocean magnetic results to date shows that much valuable information regarding the secular variation over the oceans has been obtained. It also emphasizes the lack of such information in the important north and south polar regions and in certain parts of the major oceans. It is hoped that the ocean magnetic and electric survey work of the *Carnegie* may be resumed at an early date, to round out and complete the work already done.

15. Effects of a total solar eclipse on the earth's magnetic and electric fields. J. P. AULT, Carnegie Institution of Washington.—The variation in the earth's magnetic field during a solar eclipse predicted by theoretical considerations has been verified to a remarkable degree by the observational results. Since Dr. Louis A. Bauer's first attempt in 1900 to determine this effect, much valuable information has been obtained. The conclusion seems to be justified that the screening of a part of the sun's radiation from the earth's atmosphere, due to the moon's presence between the sun and the earth, interrupts the march of the usual daily variation in the earth's magnetic field. The effect, though quite small, has been positively identified

in cases when conditions were favorable, for example, absence of cosmic magnetic storms. The magnitude of the effect depends upon the length of maximum obscuration, distance from the belt of totality, and position of the station in the portion of the earth covered by sunlight at the time of the eclipse. The variations in the earth's electric field during a solar eclipse are much more pronounced than the magnetic variations, but have not as yet been sufficiently explained by theory. The conductivity of the air increases from 10 to 20 per cent and the potential gradient decreases a like amount.

16. Interference phenomena with a thick glass plate in the path of one of the interfering beams. W. N. BIRCHBY, California Institute of Technology.—(1) With 60mm of glass in one path, compensated by air, as many as 2500 circular "white-light fringes" may be counted. (2) When the fringes were analysed spectroscopically, the spectrum was seen to be crossed by a system of dark bands in the form of complete ovals, which moved across the spectrum from the red to the violet, as the path which contained the glass was shortened. (3) With a combined source of strong sodium light and weak white light, the fringes passed through 40 or more maxima in a range of about one millimeter of path. (4) A graphical and mathematical analysis of these phenomena is given.

17. A method for comparing the rates of mixing of two liquids. L. E. DODD, University of California, Southern Branch.—The present method is an adaptation of the scattering of light rays by the striae present during the mixing of liquids. Instead of observing the striae directly, or their shadows or images projected to a screen, they are permitted to spoil the definition in a real image. The rays entering this image traverse the liquids during the mixing process. Light from a concentrated source passes through the glass mixing tank, and a real image of the source is formed on a screen by a long focus lens. The aberrations impressed upon the rays by the striae either render the image invisible, or, especially as the mixing approaches completion, cause it to "boil," like a star image seen in a telescope through an unsteady atmosphere. Cessation of the boiling fixes the time of disappearance of the striae with considerable precision. Preliminary results are given for carbon bisulphide and gasoline, with constant rate of stirring and total volume of the two liquids when mixed in various proportions. Possibly greater precision will be gained by photographing the real image with a moving film.

18. The physical characteristics of diplacusis. V. O. KNUDSEN and GEO. E. SHAMBAUGH, University of California, Southern Branch.—The writers have investigated ten cases of diplacusis, employing a vacuum tube oscillator with appropriate receivers and switching devices for measuring the displacement of pitch perception. In all ten cases the diplacusic effect was limited to one ear. Seven of the ten were characterised by the affected ear hearing too high; three of the ten heard too low. The amount of the displacement of pitch perception varied from slightly less than a semi-tone interval to nearly an octave in one instance. The effect extended over the entire tonal range, from 50 d.v. to 4800 d.v., in six of the cases; it extended only over a portion of the range in two of the cases; and the effect was uncertain over a portion of the lower range in the other two cases. The investigation furnishes convincing evidence that each ear has its own pitch-perceiving mechanism. The data are all easily explained on the assumption that the membrana tectoria, or some similar vibrating structure, responds to sound vibrations by the principle of physical resonance, and that the inertial or elastic characteristics of this structure have suffered a change in the diplacusic ear.

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